

The application of advanced oxidation with the Fenton's reagent and air stripping combined in the treatment of tar water from the biomass gasification

Łukasz GOŚCINIAK* – Institute of Chemistry, Warsaw University of Technology, Plock, Poland

Please cite as: CHEMIK 2016, 70, 4, 209–218

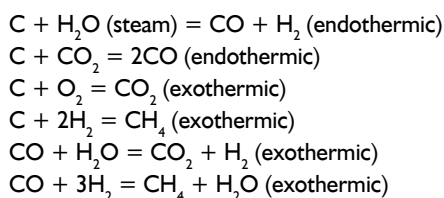
Introduction

The processes of biomass thermal conversion focused on generating energy and resources for chemicals syntheses are still a popular topic of scientific research around the world. They are perceived as a renewable and ecological source of resources for the various branches of chemistry and energy production, resulting in an unwavering attention for the technologies of e.g. biomass gasification [1].



Fig. 1. Major, renewable resources used in the process of gasification

The process of a gasification is carried out in order to obtain a gas consisting mainly of CO, CO₂, H₂, N₂, H₂O and CH₄. It is a set of transformations taking place in the conditions of elevated temperature with the presence of a gasification agent (e.g. oxygen, air, steam or carbon dioxide), which results in acquiring the gas mentioned above from solid fuels. During the process of gasification both exothermic and endothermic reaction occur, and its simplified course can be described as follows [2-4]:



Gas acquired in this way is known as the synthesis gas or the syngas, and it finds many uses in various branches of industry. It can be used as a resource for chemical synthesis (e.g. the Fisher-Tropsch process), the production of dimethyl ether or methanol, as well as a fuel for the water or steam boiler burner unit. Eventually, after foregoing a deep purification it can be burned in an engine or in a gas turbine. Syngas can also be used for the production of hydrogen or SNG (Substitute Natural Gas) – a gas with the properties of a natural gas [2-3].

Corresponding author:

Łukasz GOŚCINIAK – M.Sc, e-mail: gosciniak@pw.plock.pl

Due to the type of the converted material or the aim of a syngas production, various technological solutions concerning the gasification reactors or gas purification systems appear. Despite high differentiation, the common feature of biomass gasification processes is still the generation of side products like mineral residues, tars or the tar water [5].

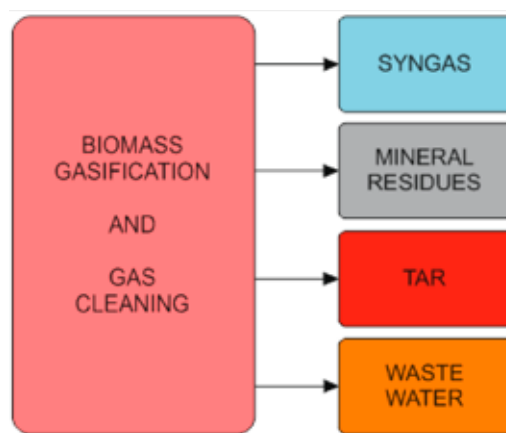


Fig. 2. Products of the biomass gasification [5]

In case of mineral residues, it is possible to use them as a mineral fertilizer for fields [6-7]. For the tars extracted from the stream of products, they can be returned to the gasification reactor as a gasification resources, and with the use of appropriate parameters of the process, it is possible to reduce their amount in the syngas [3].

The problem of waste water is connected to the presence of water in the resources, the use of steam as a gasification reagent, the specifics of the process itself (pyrogenous water), and also to the applied method of the syngas purification [1].

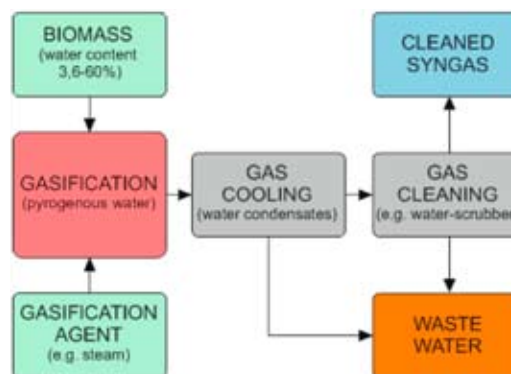


Fig. 3. The potential sources of the tar water coming for the thermal process of the biomass conversion [5, 8]

The water fraction coming from the biomass gasification installations is a complex mixture of physical pollutions and various chemical substances. Depending on the factors mentioned above, it can contain tars, suspended solid particulates, acetic acid, methanol,

ammonia, sulphides, phenols or polycyclic aromatic hydrocarbons, and also insoluble substances in a emulsified form. For example, over 150 various chemical compounds have been found in a samples of tar water obtained during the gasification of alder wood chips.

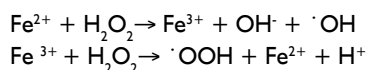
Table I
Exemplary compounds found in tar water from the gasification process [2]

Parameter	Sample I	Sample II
	%weight	
Water content	78.19	85.99
Total amount of volatile organic compounds (estimated)	~6	~7
Dust content	0.67	0.36
Tars insoluble in water	4.82	2.29
Acetic acid	2.81	4.82
Acetaldehyde	0.07	0.03
Methanol	0.937	0.535
Benzene	0.0079	0.0031
Phenol	0.149	0.090
2,4-dimetylophenol	0.049	0.027
Naphthalene	0.041	0.017
2-furaldehyde	0.208	0.140

It has to be mentioned that the majority of compounds which can be found in the tar water is significantly toxic and immune to degradation. Due to this, the tar water from the gasification process has to be properly treated before it can be transported to natural water reservoirs in order to avoid endangering the environment. The technology of biomass conversion is still under development, and as a result, there are still ongoing researches trying to come up with an effective and economic method of dealing with this problem. The solution for it may become a crucial factor, deciding about the further development and spread of the biomass gasification technology [2].

When it comes to the tar water treatment, depending on the type and the level of the pollution, there are different mechanical, psychochemical and biological methods that can be used. A set of different parameters is what decides on the applied method. The most common among them are Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). Typically, those methods used individually do not provide an adequate level of the tar water purification. In accordance to that, there is an increasing interest in hybrid solutions, meaning e.g. combining the methods of Advanced Oxidation Processes (AOP) with membrane technologies, adsorption technologies, and other [9].

The core of advanced oxidation methods is the use of strong oxidants, e.g. ozone, hydrogen peroxide or hydroxide radicals ($\cdot\text{OH}$) to decay the substances contained in the tar water. The oxidation potential of the hydrogen peroxide and hydroxide radicals ($\cdot\text{OH}$) is considered as one of the highest among the known oxidants, resulting in a very high reactivity and effectiveness in the oxidation of various chemicals. While there are various methods of generating hydrogen radicals, one of the simplest is the use of so called Fenton's reagent, a mixture of H_2O_2 and Fe^{2+} ions. In this reaction the radicals are created as a result of catalytic decay of hydrogen peroxide as it follows [10].



Hydroxide radicals ($\cdot\text{OH}$) react with almost all pollutions (e.g. they oxidate alcohols do ketones) present in the tar water. It is highly probable that additional oxidations also appear, namely, a direct oxidation with hydrogen peroxide, an oxidation with radicals generated beyond the

reaction stated above, as well as, an oxidation with halide radicals coming from the reaction of hydrogen radicals ($\cdot\text{OH}$) with a majority of halide ions (Cl^- , Br^-), which may lead to a total mineralization of pollutions [11 - 12]. In optimal conditions, the Fenton's reagent oxidizes many complex compounds with more than a effectiveness higher than 90%. The Fenton's reaction can be perceived as an effective method also in reducing the amount of pollutions in the tar water coming from the biomass gasification [1]. One of the advantages of this process, in contrary to different methods, and despite its high effectiveness, is its simplicity. It does not require specialist equipment, it is homogenous (resulting in no limitations regarding the mass transmission), and the reagents are widely available. Moreover, it is also effective in the case of tar waters with a high turbidity. Although, one of its flaws is the necessity of correcting the final reaction of the tar water [11, 13-14]. Similarly to different methods of AOP, the price of oxidants may be considered as a limitation. Nevertheless, the progress in increasing their effectiveness and reducing the cost of use, together with increasing requirements concerning the environment protection, foster the use of AOP in a wider range. What is more, while combined with other methods (e.g. stripping), they show a synergetic effect which allows to achieve increased effectiveness in pollution removal [9].

Stripping is a process of the mass transfer, a physical method of purification, which aim is to eliminate a gas dissolved in water (e.g. CO_2 , H_2S), as well as, organic volatile substances [14]. Its core are the processes of desorption, conducted e.g. in a stream of a neutral gas (proper desorption). In this case, a stream of a neutral gas, most frequently a steam or nitrogen, flows through the tar water. As a result, organic volatile substances dissolved in the tar water are removed from it, and then change to a vapour phase because their particles pressure above the solution is higher than in the gas mixture. This process is conducted in packed columns or columns with a sparger, where liquid is flowing in the top and the vapour phase enters from the bottom. Then the treated solution flows out of the bottom, and the vapour phase in a mixture with the neutral gas is removed out of the top of the column [15]. The effectiveness of the process can be achieved by increasing the amount of contact area between the phases, which can be done by spraying the water or decreasing the size of gas bubbles. A special structured packing is also used, resulting in a constant splashing of water droplets during the process. Due to it, a decrease of the surface tension, which is the smallest during the renewed formation of the droplets, can be observed [16].

Experimental Part

The aim of this paper was to define whether the air stripping process turned out to be helpful in the treatment of tar water coming from the biomass gasification or not. The research material consisted of four tar water fractions, among which first one had undergone an additional filtration process resulting in the sample Ia. Those samples of the tar water were characterized by different properties, depending on used methods of the syngas purification, with one common trait in the form of a very high level of pollution described with the Chemical Oxygen Demand.



Fig. 4. Tar waters from the biomass gasification installation

Table 2

Chosen psychochemical properties of examined tar water samples

Parameter	Tar water no.1	Tar water no.2	Tar water no.3	Tar water no.4
pH	5.0	4.6	4.4	3.8
Conductivity, mS/cm	4.0	6.4	6.1	3.4
COD, mg O ₂ /dm ³	46276	30087	95367	75717
Turbidity, NTU	> 1000	> 1000	66	> 1000
Suspensions content, mg/dm ³	> 750	> 750	68	> 750
Colour	black and brown	dark brown	orange	dark brown
Odour	sharp, choky, smoky	burning wood	gas oil	choky, smoky

As a part of this paper, a gas stripping installation in the laboratory scale, allowing to conduct the stripping process and combine it with advanced oxidation methods has been built. Based on conducted tests, a method of air dispersion granting the best development of gas bubbles has been decided. Also, an initial research aiming to evaluate the validity of tar water stripping has been conducted. Due to the level of a gas dispersion, and the presence of solid pollutions in certain samples, the use of the barbotage via a sparger was decided as the most optimal method of the air stripping. It has provided the best degree of air bubbles dispersion. Moreover, in contrary to perforated dividers or Bialecki rings the sparger did not clog with the particles suspended in the tar water.

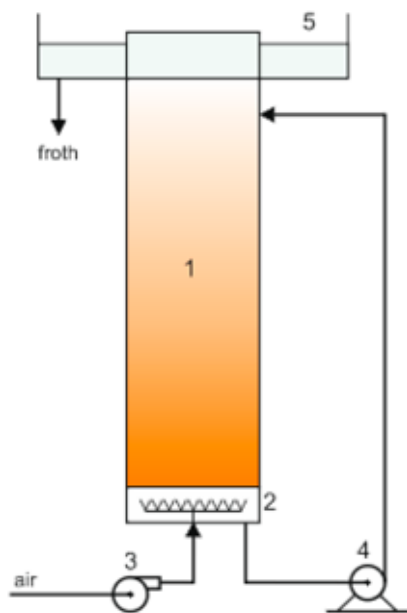


Fig. 5. Scheme of a stripping column: 1 – stripping column, 2 – sparger, 3 – membrane pump, 4 – circulating pump, 5 – froth receiver

The process of tar water treatment

At the beginning, an adequate amount of a raw tar water together with a tar water combined with the hydrogen peroxide or a tar water with the Fenton's reagent was added to a stripping column made of an acid-proof steel, equipped with a sparger. Then it had undergone the process of aeration via a membrane pump. The liquid phase was transferred from the bottom of the column to the top with the use of a circulation pump in order to achieve a counter current flow of the phases. The froth generated during the process, together with the pollutions it contained, was received at the top of the column.

Before the stripping, the correction of pH was not necessary, as the tar water pH was oscillating between 3 and 6 units, meaning the most effective range for the processes of oxidation.



Fig. 6. Solid pollutions inside the froth

In order to define the influence of a process duration on the level of purification (in cases of using the stripping process, as well as, without it) after 5, 25, and 60 minutes of the process different samples of tar water were taken and had their COD levels examined. In order to obtain information about the influence of an air stripping on the effectiveness on AOP, processes of the advanced oxidation without the barbotage were conducted simultaneously.

Each of 4 samples of the tar water underwent:

- **S** – air stripping. To achieve that, 200 cm³ of a raw tar water was put into a stripping column and with the use of a sparger was aerated for 60 minutes.
- **F** – tar water oxidation with the use of the Fenton's reagent without the aeration. In order to achieve that, 0.4 g of a crystalline FeSO₄·7H₂O was added to the beaker containing 200 cm³ of a raw tar water, and then mixed via a magnetic stirrer till the salt's total dissolution. Afterwards, 10 cm³ of a 30% hydrogen peroxide was added to the solution and then the mixture was stirred for 60 minutes.
- **SF** – air stripping combined with the advanced oxidation with the use of the Fenton's reagent. In order to achieve that, 0.4 g of a crystalline FeSO₄·7H₂O was added to the beaker containing 200 cm³ of a raw tar water, and then mixed via a magnetic stirrer till the salt's total dissolution. Afterwards, 10 cm³ of a 30% hydrogen peroxide was added to the solution, and then the mixture has been transferred to a stripping column and aerated with the use of a sparger for 60 minutes.

The first sample underwent also the process of oxidation with the use of peroxide alone (**U**), however, achieved levels of COD reduction were slight. Probably, it is connected to the definitely lower than hydroxide radicals oxidation potential of the peroxide and a longer duration of the reaction. Due to a relatively low effectiveness when compared to the Fenton's reagent, this method of the oxidation was abandoned in the further part of this research.

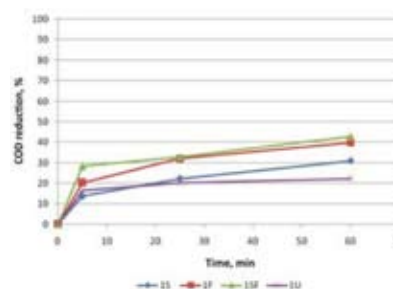


Fig. 7. COD reduction diagram [%] for the tar water no. 1

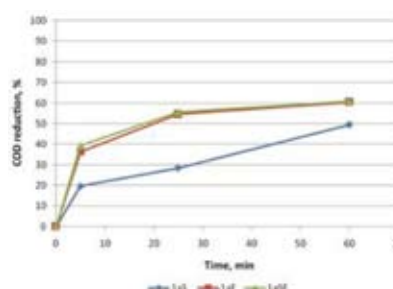


Fig. 8. COD reduction diagram [%] for the tar water no. 1 after the filtration

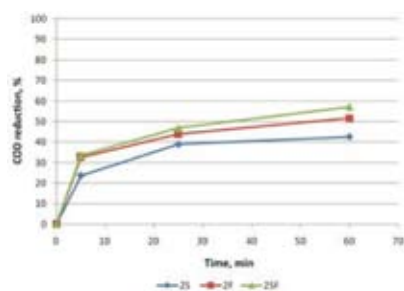


Fig. 9. COD reduction diagram [%] for the tar water no.2

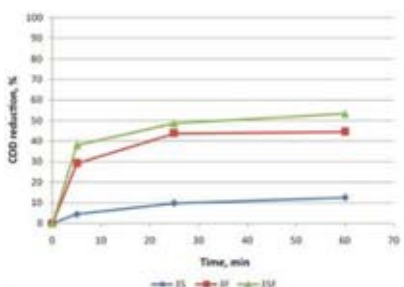


Fig. 10. COD reduction diagram [%] for the tar water no.3

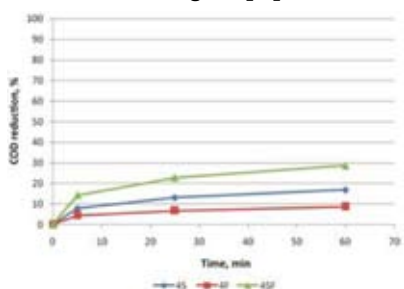


Fig. 11. COD reduction diagram [%] for the tar water no.4

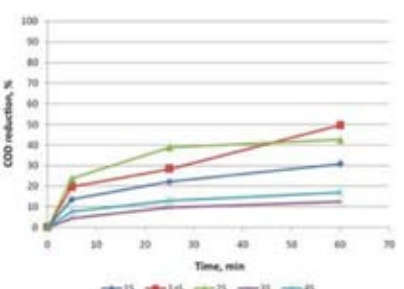


Fig. 12. COD reduction diagram [%] for tar waters after stripping

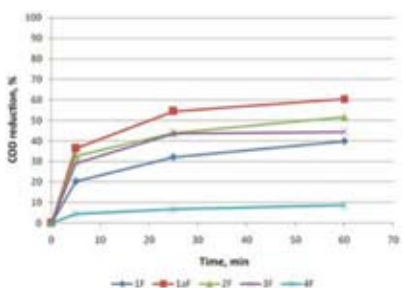


Fig. 13. COD reduction diagram [%] for tar waters after the advanced oxidation with the use of the Fenton's reagent

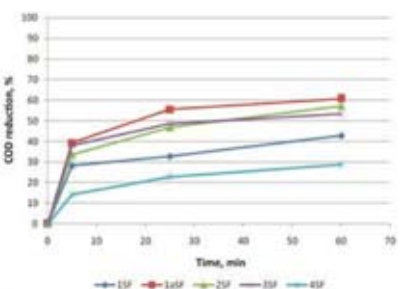


Fig. 14. COD reduction diagram [%] for tar waters after the stripping combined with advanced oxidation with the use of the Fenton's reagent

Summary

The initial results of this research indicated that the use of air stripping, especially when combined with the advanced oxidation with the use of the Fenton's reagent can be considered an effective method of a pre-treatment of the tar water coming from the biomass gasification installations.

The air stripping process allowed the reduction of the amount of pollutions in every sample (measured by the COD indicator), yet it has to be mentioned that its effectiveness was not identical for all of them. This process was the least effective in the sample no.3 with reducing the COD by 13%, while the highest effectiveness in the amount of almost 50% was observed in the sample no.1 (which underwent an additional filtration before the process of a stripping took place). It can be connected to the fact, that majority of the solid suspensions were extracted during the filtration, and the remaining ones were removed with the froth. This additional effect of a flotation was also observed in remaining samples.

In case of the tar water oxidation with the use of peroxide alone, the effectiveness in the COD reduction was slighter when compared to the Fenton's reagent. Due to a lower than hydroxide radicals oxidation potential of peroxide, the oxidation processes required more time and had a lower effectiveness. With the stated parameters of the process, peroxide was not able to react fully or react at all with the pollutions present in the tar water sample.

In all examples of the oxidation, the highest COD reduction was observed during the initial phase of the process. An intense course of this reaction can be also confirmed by a sudden increase in the temperature.

When it comes to combining the advanced oxidation with the use of the Fenton's reagent with the air stripping, favourable effects of the purification levels were observed. As a result of using the Fenton's reagent or the Fenton's reagent combined with the air stripping, it was possible to reduce characteristic odours of the tar water to a significant degree.

During the process of the stripping (and to some extent also in the process of the oxidation) a generation of the froth removing the solid suspensions, thus, increasing the effectiveness of the tar water treatment, was observed, especially during the initial phase of the process. However, in the case of sample no.4, the amount of the froth was so immense that it was hard to conduct the process.

The use of air stripping, especially when combined with the oxidation with the use of the Fenton's reagent can be considered as an effective method of pre-treating the tar water coming from the biomass gasification installations. Due to a possibility for an increased effectiveness of used tar water treatment methods by e.g. the optimisation of the air flow, the amounts of hydrogen peroxide or Fe^{2+} , as well as, pH or the temperature of the environment, further research should be conducted.

Literature

- Gościński Ł.: Zastosowanie nadtlenu wodoru w oczyszczaniu wody odpadowej z procesu termicznej konwersji biomasy. w Wybrane problemy naukowo-badawcze chemii i technologii chemicznej. "DRUKARNIA" Sp. z o. o. Sierpc, 2013, 161-171
- Fitko H., Stelmach S.: Charakterystyka wody pogażowej otrzymanej przy zgazowaniu biomasy. Instal 2013, 6, 22-25
- Piskowska-Wasiak J.: Oczyszczanie i przetwarzanie gazu ze zgazowania biomasy w celu wytworzenia SNG (Substitute Natural Gas). Nafta-Gaz 2011, 5, 347
- Franco C., Pinto F., Gulyurtlu I., Cabrita I.: The study of reactions influencing the biomass steam gasification process. Fuel 2003, 82, 839
- Gościński Ł.: The Application of Coagulation and Advanced Oxidation Processes Combined in the Treatment of Tar Water from Biomass Gasification. Applied Mechanics and Materials 2015, 797, 369-376
- Wisn J., Matwiejew A.: Biomasa – badania w laboratorium w aspekcie przydatności do energetycznego spalania. Energetyka 2015, 9, 639

7. Kowalczyk-Juško A.: *Popiół z różnych roślin energetycznych*. Proceedings of ECOpole 2009, **3**, 159
8. [8] Lettner F., Timmerer H., Haselbacher P.: *Biomass gasification – State of the art description*, Graz University of Technology - Institute of Thermal Engineering Inffeldgasse Austria 2007, 48
9. HYPERLINK <http://ecomanager.pl/poglebione-utlenianie-w-oczyszczaniu-sciekow/> (19.02.2016)
10. Kardasz K., Kędzierska E., Konopka M., Majzner M.: *Opracowanie założeń do projektu oraz projektu procesowego węzła utylizacji ścieków technologicznych*, Sprawozdanie z pracy naukowo-badawczej, 2000, 3-4
11. Barbusiński K.: *Oczyszczanie ścieków przemysłowych metodami katalitycznymi wykorzystaniem nadtlenu wodoru*. Chemik 2001, **2**, 31-36
12. Lewkiewicz-Malysa A., Rogowska-Kwas R., Winid B.: *Reduction of hydrocarbon contaminations in the chemical oxidation process*. Czasopismo Techniczne 2008, **2**, 250
13. Nawrocki J.: *Zaawansowane procesy utleniania w oczyszczaniu wody*. Ochrona środowiska 1999, **3**, 31-34
14. HYPERLINK <http://www.pulawy.com/314-informacje-rynkowe---szczegoly/lang/pl-PL/infoid/845/list/242/default.aspx> (19.02.2016)
15. Kowal A. L., Świdorska-Bróz M.: *Oczyszczanie wody. Podstawy teoretyczne i technologiczne, procesy i urządzenia*. PWN, 2007, **94**, 613
16. Planowski A. N., Ramm W. M., Kagan S. Z.: *Procesy i aparaty w technologii chemicznej*. WNT, Warszawa, 1974, 611
17. Piekutin J.: *Usuwanie związków ropopochodnych z wody*. Rocznik Ochrona Środowiska 2013, **15**, 2470

*Łukasz GOŚCINIĄK – M.Sc., (Eng.), acquired his Master's degree in Chemical Engineering in 2008 at the Faculty of Civil Engineering, Mechanics and Petrochemistry at Warsaw University of Technology (WUT). Currently employed at Warsaw University of Technology, Institute of Chemistry.
e-mail: gosciniak@pw.plock.pl, phone: +48 24 36 72196

Aktualności z firm

News from the Companies

Dokończenie ze strony 213

Zmiany w Radzie Nadzorczej Grupa Azoty Kopalnie i Zakłady Chemiczne Siarki „Siarkopol” SA

30 marca br. odbyło się Nadzwyczajne Walne Zgromadzenie Grupy Azoty Kopalnie i Zakłady Chemiczne Siarki „Siarkopol” SA, podczas którego zostały podjęte uchwały zmieniające skład Rady Nadzorczej Spółki V kadencji.

W dniu 29.03.2016 r. rezygnację z funkcji Członka Rady Nadzorczej złożył Pan Witold Szczypiński. Decyzją Nadzwyczajnego Walnego Zgromadzenia ze składu Rady Nadzorczej odwołany został Członek Rady Nadzorczej Pan Wojciech Naruć.

Do składu Rady Nadzorczej powołani zostali: Pan Jerzy Koziaara na Przewodniczącego Rady Nadzorczej oraz Członkowie Rady Nadzorczej Panowie: Grzegorz Piątkowski oraz Witold Jan Brodalka.

W obecnym składzie Rady Nadzorczej pozostają: Wiceprzewodnicząca Rady Nadzorczej Pani Barbara Haraburda oraz wybrani z ramienia pracowników Panowie Andrzej Kaplan i Sławomir Krawczykowski. (abc) (<http://grupaaazoty.com/pl/wydarzenia/30.03.2016>)

Zmiana w radzie nadzorczej producenta kauczuków

Zarząd spółki Synthos poinformował, iż 4 kwietnia 2016 r. wpłynęło oświadczenie o rezygnacji z członkostwa w radzie nadzorczej jej wiceprzewodniczącego, Krzysztofa Kwapisza. Rezygnacja została uzasadniona względami zdrowotnymi i będzie skutkować z dniem odbycia najbliższego Walnego Zgromadzenia Akcjonariuszy. Po ustąpieniu Kwapisza w skład rady nadzorczej Synthosu wchodzi: Jarosław Grodzki (przewodniczący), Grzegorz Miroński (sekretarz), Robert Oskard i Wojciech Ciesielski (członkowie). (kk) (<https://www.plastech.pl>, 5.04.2016)

Zmiany w składzie Zarządu Grupy Azoty Puławy

Rada Nadzorcza Grupy Azoty Puławy podczas posiedzenia 5 kwietnia 2016 r. dokonała zmian w składzie Zarządu. Zgodnie z podjętą uchwałą nowym p.o. Prezesa Zarządu spółki Grupa Azoty Zakłady Azotowe Puławy SA został Mariusz Bober, pełniący również funkcję Prezesa Zarządu Grupy Azoty SA To strategiczna decyzja, która usprawni sposób zarządzania Grupą Azoty oraz przyczyni się do jej głębszej integracji.

Rada Nadzorcza podjęła również decyzję o rozszerzeniu składu Zarządu. Nowymi Wiceprezesami Zarządu zostali Panowie: Zbigniew Gagat i Jacek Janiszek.

Ciągły rozwój i wzrost innowacyjności to priorytety Grupy Azoty SA Bezpieczeństwo w tym zakresie zapewni dalsza integracja Grupy. Dlatego, mając na uwadze cele strategiczne Grupy, Rada Nadzorcza powierzyła dziś Prezesowi Zarządu Grupy Azoty SA Panu Mariuszowi Boberowi dodatkową funkcję p.o. Prezesa Grupy Azoty Puławy.

Decyzja ta ma strategiczne znaczenie dla dalszego rozwoju całej Grupy Azoty. „Puławy” to największa spółka w grupie o kluczowym znaczeniu – dlatego powierzenie Prezesowi całej Grupy Azoty zarządzania tą Spółką przyczyni się głębszej integracji na drodze do celu jakim jest dalszy rozwój Grupy, zarówno na polskim, jak i europejskim rynku.

Sprawujący do tej pory swoje funkcje Prezes Zarządu – Marian Rybak oraz Wiceprezes Zarządu – Zenon Pokojski zostali zawieszni w pełnieniu obowiązków.

W składzie Zarządu pozostał Wiceprezes Zarządu Pan Wojciech Kozak, wybrany z ramienia pracowników. Jego mandat wygaśnie z dniem odbycia Zwyczajnego Walnego Zgromadzenia Akcjonariuszy Grupy Azoty Puławy.

P.o. Prezesa Zarządu spółki Grupa Azoty Zakłady Azotowe Puławy SA Pan Mariusz Bober podjął decyzję o niepobieraniu wynagrodzenia z tytułu pełnienia funkcji w Grupie Azoty Puławy. (abc) (<http://grupaaazoty.com/pl/wydarzenia/6.04.2016>)

Prof. Maciej Chorowski pokieruje NCBR

Narodowe Centrum Badań i Rozwoju ma nowego dyrektora. Został nim prof. dr hab. inż. Maciej Chorowski. Wicepremier Jarosław Gowin przedstawił nowego dyrektora podczas konferencji prasowej w Ministerstwie Nauki i Szkolnictwa Wyzszego. Prof. Chorowski jest profesorem nauk technicznych, kierownikiem licznych projektów badawczych i autorem dziesiątek prac naukowych. Zawodowo jest związany z Politechniką Wrocławską. (kk) (<http://www.ncbr.gov.pl/>, 8.04.2016)

Dokończenie na stronie 228