WYDAWNICTWO SIGMA-NOT

POLISH TECHNICAL REVIEW

4/2020

SCIENCE AND INDUSTRY IN A COUNTRY OF CHANGES

Open Access www.polishtechnicalreview.com e-ISSN 2657-6716 WYDAWNICTWO *SIGMA-NOT* www.sigma-not.pl since 1964

HYDROGEN – BUILDING MATERIAL OF THE UNIVERSE, EARTH ANOMALY OR COMMONLY AVAILABLE FUEL?

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POLISH TECHNICAL REVIEW

SCIENCE AND INDUSTRY IN A COUNTRY OF CHANGES

TITLE OWNER/WŁAŚCICIEL TYTUŁU:
National Council of Federation of Engineering Associations NOT
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Czackiego Street 3/5, 00-043 Warsaw
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www.enot.pl, e-mail: sekretariat-prezes@not.org.pl

PUBLISHER/WYDAWCA:

WYDAWNICTWO *SIGMA-NOT*

SIGMA-NOT Publishing House Ltd.
Wydawnictwo Czasopism i Książek Technicznych
SIGMA-NOT Spółka z o.o.
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DTP COMPOSITION/SKŁAD I ŁAMANIE:
SIGMA-NOT Publishing House Ltd.
Wydawnictwo Czasopism i Książek Technicznych
SIGMA-NOT Spółka z o.o.
Ratuszowa Street 11, VII p., 03-450 Warsaw
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www.sigma-not.pl
e-mail: sekretariat@sigma-not.pl

OPEN ACCESS QUARTERLY e-ISSN 2657-6716 SINCE 1964

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Marry Christmas,
may your christmas
be filled with health,
lots of happiness and joy.

May this Coming Year
bring health and happines to you
and your family.

Marry Christmas and Happy New Year 2021!

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DOI: 10.15199/180.2020.4.1

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HYDROGEN – BUILDING MATERIAL OF THE UNIVERSE, EARTH ANOMALY OR COMMONLY AVAILABLE FUEL?

WODÓR – BUDULEC WSZECHŚWIATA, ZIEMSKA ANOMALIA CZY POWSZECHNIE DOSTĘPNE PALIWO?

Summary: *Hydrogen is a carrier and energy store. It is becoming the energy supplier. The global energetic-climatic policy forces us to search for the alternative solutions and the sources of cheap electric energy. The implementation of RES (renewable energy sources) and the consequent legal regulations runs laboriously while the hydrogen revolution (although still ineffective) is developing dynamically and gives a chance to stabilization of the situation in energy storage, inter alia, in Poland and will make the pro-ecological activities real. Constantly increasing participation of hydrogen in energy sector, especially in global approach, forces the leading electric energy producers to increase the additional financing of the mentioned research sectors.*

Unfortunately, the development of hydrogen infrastructure is slow. It is inhibited by a lack of the need (that is, still too low demand) and the prices of hydrogen for final users are highly dependent on, for example, the number of refuelling.

The utilization of hydrogen for carbonization purposes requires, however, it obtaining in an emission-free way. At present, the discussed raw material, being mainly used in refinery and chemical industry, is generated almost exclusively in the processes of steam reforming of natural gas or coal re-gasification. The both mentioned methods are connected with CO_2 emission, therefore, the product, obtained in this way, is called grey hydrogen. On the other hand, electrolysis is the non-emission generating method; it needs only water and electric energy from the renewable sources.

The global energetic-climatic policy forces us to search for alternative solutions and for new sources of cheap electric energy. Aspects of storage and transmission of hydrogen in the industrial scale and optimization of the process of its obtaining (production?) seem to be a priority. We know what hydrogen is, we know its properties, we are able to accumulate and transform it in electric energy. The ideas of its storage are dynamically developing.

We hope that after reading this research paper, the question will be generated in the mind of the reader: when "the outbreak of the hydrogen era" is expected? In our opinion, the mentioned period was commenced at the second decade of 21st century. A lot of articles concerning the possibility of utilizing the mechanical vehicles, driven by hydrogen, the planned stations of hydrogen refuelling or construction of underground storehouses of H_2 in salt caverns are the premis.

Keywords: *hydrogen, energy carrier, storeage, decarbonisation, emission, cavern, energetic raw material*

Streszczenie: *Wodór to nośnik, magazyn energii. Staje się dostawcą energii. Światowa polityka energetyczno-klimatyczna zmusza do szukania alternatywnych rozwiązań i źródeł taniej energii elektrycznej. O ile wdrażanie polityki OZE i idących za nią regulacji prawnych przebiega żmudnie, o tyle rewolucja wodorowa (choć ciągle nieefektywna) rozwija się dynamicznie i daje szanse na ustabilizowanie sytuacji magazynowania energii m.in. w Polsce oraz urzeczywistni działania proekologiczne. Wciąż wzrastający udział wodoru w sektorze energetycznym szczególnie w ujęciu globalnym, zmusza czołowych producentów energii elektrycznej do zwiększenia dofinansowania tych sektorów badawczych.*

Niestety rozwój infrastruktury wodorowej jest powolny. Hamuje go brak potrzeby (czyli ciągle zbyt niski popyt), a ceny wodoru dla konsumentów końcowych są wysoce zależne na przykład także od liczby tankowań.

Wykorzystywanie wodoru w celu dekarbonizacji gospodarki wymaga jednak pozyskiwania go w sposób niegenerujący emisji. Obecnie surowiec ten, używany głównie w przemyśle rafineryjnym i chemicznym, powstaje niemal wyłącznie w procesach reformingu parowego gazu ziemnego lub regazyfikacji węgla. Obie metody wiążą się z emisją CO_2, dlatego wytwarzany w ten sposób produkt określono jako szary wodór. Niegenerującą emisji metodą jest natomiast elektroliza, do której potrzebne są woda oraz energia elektryczna z odnawialnych źródeł.

Światowa polityka energetyczno-klimatyczna zmusza do szukania alternatywnych rozwiązań i źródeł taniej energii elektrycznej. Priorytetowe zdają się być aspekty magazynowania i przesyłu wodoru na skalę przemysłową oraz optymalizacja procesu jego otrzymywania (produkcji?). Wiemy czym jest wodór, znamy jego właściwości, potrafimy zgromadzić i przeobrazić w energię elektryczną. Idee jego magazynowania rozwijają się w dynamicznym tempie.

Mamy nadzieję, że po lekturze tekstu w umyśle Czytelnika zrodzi się pytanie, kiedy nastąpi „wybuch ery wodoru". W naszej opinii ten okres rozpoczął się w drugiej dekadzie XXI wieku. Setki artykułów dotyczących możliwości wykorzystania pojazdów mechanicznych napędzanych wodorem, planowanych stacji tankowania wodoru czy budowy podziemnych magazynów H_2 w kawernach solnych to przesłanka.

Słowa kluczowe: *wodór, nośniki energii, magazynowanie, dekarbonizacja, emisja, kawerna, surowiec energetyczny*

Introduction

Hydrogen is a chemical element with atomic number of 1. It is one of the most universally found elements on our Globe. The most frequent isotope of hydrogen is atom, consisting of one proton and one electron. As a standard, gas hydrogen occurs in a molecular form H_2. It is colourless, without taste or smell. It is easily flammable and is not toxic. It burns without a visible flame; the water vapour is the effect of its combustion.

If we want to write about hydrogen which is, together with helium, the main building material of our "surroundings" we should enter for a moment into a world of cosmology, construction of the Universe and realize that 95% of the Universe surroundings are made of black energy and black matter and the remaining 5% are galactic together with the Milky Way, stars, inter-galactic gas and our Solar System, including our old Planet – which seems to be the evident phenomenon, a special case, not to say anomaly. The known matter, including neutrino consist only 1%

of the mass of Cosmos; the remaining 4% include hydrogen and helium. Pure hydrogen and pure helium; it has a great energetic significance.

The probability calculus will tell us that our Solar System, Earth is many times repeatable but in the vastness of the Universe, it is the anomaly. It is perhaps more than anomaly, it is better to define it as a peculiar case because hydrogen on the earth is entrapped in the hydrocarbon and nitrogen (ammonia – NH_3 compounds) and in water. In the contrary to the Cosmos, it does not occur independently in the earthly nature.

Hydrogen is a carrier, the energy store. It becomes the supplier of energy when – in the processes of nuclear synthesis (the processes occurring, for example, on the Sun) – as a result of combination of hydrogen atoms in enormously high temperatures, it becomes a building material of helium, when releasing simultaneously enormous quanta of energy and free neutrins. Apart from the gravitation energy, the thermonuclear reaction is the main source of the Sun energy, the energy of stars. The inhabitants of the Earth are far from the possibility of controlling the mentioned process; we have learned only destruction in a form of hydrogen bomb.

The meaning of the word "HYDROGEN" is "forming water" – two atoms of hydrogen and one atom of oxygen strongly connected together. Hydrogen in two atoms is so-called as it "forms water". It is the enormous, earthly energetic resource, being practically unprecedented (according to the available today knowledge) in the Universe. We have also a hydrogen in a molecule in a form of ammonia NH_3, urea: $CO(NH_2)_2$ but also in methane (methane, the simplest hydrocarbon - carbon and 4 atoms of hydrogen, CH_4) and in hydrocarbons which had changed mankind during the recent century. But it is water, as being universally present in Earth, which seems to be the easier source of obtaining hydrogen. Today, the majority of hydrogen, utilized in technological processes of the European refinery, chemical and petrochemical industries is obtained, of course, from methane; it results from the fact that we have local electric energy plants and energy in a form of water vapour under the appropriate pressures and temperatures, we have available expensive catalysers which practically enable carrying out the reaction of obtaining hydrogen. The second and unfortunately, the greatest source of industrial hydrogen on Earth is a reaction of carbon and water (the mentioned reaction consists in generation of the so-called synthesis gas which gives high emissions of carbon oxide and dioxide), similarly as from methane to synthesis gas.

Water in Earth is a cosmic phenomenon, source of life, a special case or perhaps – anomaly (?) searched by the scientists in the Universe. We learned to perform electrolysis, i.e. utilization of electric current flow through pure water two hundred years ago; we are not able to improve the mentioned technology, or change in such a way that the molecule of water is separated non-expensively, quickly and effective in respect of energy. When speaking about electrolysis, we cannot forget the PEM method (Polymer electrolyte membrane), being an alternative to the less effective but cheaper method (alkaline water electrolysis). The only one but deciding weak point of PEM is its high cost. When speculating, we may try to lower the costs of the mentioned method by replacement of platinum with graphene in a role of catalyser. Hydrogen is universal building material of the surrounding Cosmos which we understand and experience. But it is not independently available on earth. It must be released and, additionally, transmitted to the place where it is necessary.

Future lies in hydrogen

Global energetic-climatic policy forces us to seek for the alternative solutions and sources of cheapo electric energy. The introduction of RES policy and the resulting legal regulations run laboriously whereas hydrogen revolution (although being still ineffective) is dynamically developing and gives a chance for stabilization of the situation in respect of energy storage, *inter alia*, in Poland; it would make the pro-ecological activities real. Constantly increasing participation of hydrogen in energetic sector, especially in global aspect, makes that the leading producers of electric energy increase the additional financing of the mentioned research sectors.

The most intensive work upon the properties of hydrogen is implemented, first of all, in the United States, Germany and France. Poland has also the achievements in this field, with its projects by Orlen/Lotos[1)], Gaz-System S.A.[2)] , in cooperation with higher education schools, *inter alia*, with AGH University of Science and Technology, Warsaw University of Technology and the Silesian University of Technology. A wide popularization of the discussed

[1)] Biznes Alert/Cire: President of PGE Wojciech Dąbrowski said that the company observes hydrogen technology; however, it does not intend to invest in it at this moment, as it is too expensive still. The president was asked about the application of hydrogen in energetics. He said that [...] this technology is still very expensive. It is still a lot of work, efforts in order to decrease the price to the level acceptable by our customers. The application of hydrogen in heating, in energetics would unprofitable for them. We are striving at reduction of charge from our customers. Dąbrowski did not exclude that in the future, the discussed technology would find the application in energetics. –"Our turbines in the constructed gas blocs in Power Plant Dolna Odra (Lower Oder River) would be adapted to combustion of gas with admixture of hydrogen. At present, there is no possibility to have the discussed fuel universal and available at the acceptable price. It is still connected with the high costs"

[2)] On 14 September 2020, the information appeared that the European Commission approved the application for accession of Gaz-System to the European Clean Hydrogen Alliance – ECH2A. It is a successive initiative, after signing the letter of intention (July 2020) about establishing the partnership in favour of building hydrogen economy in Poland, with the involvement of Gaz-System Company. The European Clean Hydrogen Alliance was established by the European Commission with the aim to support implementation of the investment and establish hydrogen economy in the European Union in accordance with the assumptions of the European Hydrogen Strategy, being published in July 2020. The Alliance is expected to play a fundamental role in the support of investment activity, carried on in the total chain of values, including production, transport, storage and utilization of hydrogen in the particular sectors of economy (e.g. transport, industry, energetics, heating system). In the case of necessity, the Alliance will undertake the activities, aiming at support of the labour market and its adaptation to the needs of local hydrogen economy. The Alliance will consist of the representatives of industry, national, regional and local authorities and the representatives of citizen society.

„Gas-System participates actively in shaping a dialogue on introduction of the assumptions of the European Green New Deal". We want to indicate, via the membership in the Alliance, how the natural gas may play a significant role in energetic transformation in Poland and in total EU. Gaz-System as the undertakes operator of transfer system, undertakes activities which may enable utilization of natural gas as low-emission energy source, supporting the implementation of the aims of climatic policy of the European Union in a long-term perspective. Besides it, Gaz-System is also strongly involved in research-developmental projects, aimed at introduction of the new methods for operation of gas infrastructure. The mentioned activities include, inter alia, adaptation of the assets for the needs of receipt and transport of renewable and decarbonised gases, including hydrogen" – citation after Tomasz Stępień, the President of the Board of Gaz-System company.

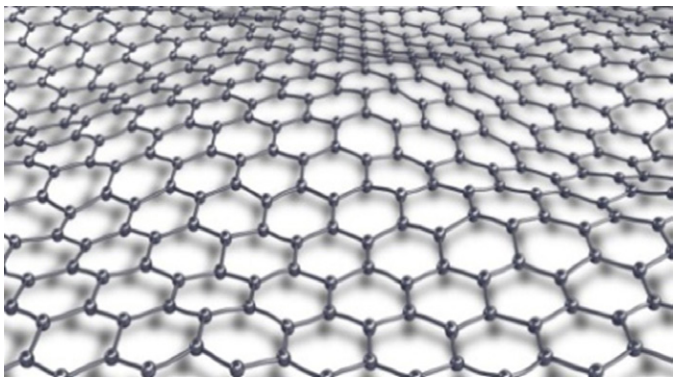
element in the Cosmos and the simple, though very expensive methods for its obtaining result in the development of energetics and rendering it a name of ecological (organic) fuel. Therefore, was the process of replacing the petroleum of natural gas inhibited until now? Whether it will be inhibited? The so-far costs of obtaining hydrogen were higher than the energy, obtained from its combustion what decided on unprofitability of the discussed process. Therefore, let's pay attention to the advantages, resulting from the increase of the hydrogen participation in the national production of electric energy. Its ecological nature, connected with the production of water (water vapour) in the process of combustion, should be confronted with the sulphur dioxide and carbon dioxide, being the by-products of fossil fuels' combustion. Moreover, hydrogen has a low ignition temperature and a relatively very high temperature of combustion in relation to the mass of the mentioned element. The cars, driven by hydrogen, are becoming more and more popular; their high performance and the application of "clean fuel" convince the users to bear higher expenses and overcome the difficulties connected the lack of fuelling station[3] [2] [3].

Aspects of storage and transfer of hydrogen in the industrial scale and the optimization of the process of its production seem to be a priority.

What may be a role of graphene in "hydrogen revolution"?

Graphene is a flat structure consisting of carbon atoms; its form resembles a thin (thickness is only one atom) plaster of wax foundation. One of its main features includes heat conductivity (thermal conductivity is equal to 4840–5300 W/mK) which is intensively employed in different industrial branches. As being a very resistant material (100 times harder than steel), it is subjected to elongation even by 25%. Graphene may play a function of a very sensitive gas detector and it is connected with its sorption properties, in which the total surface of material participates. The possibilities of applying it as insulation/dam for the smallest atoms, *inter alia*, of helium or hydrogen, is the essence of the energy storage process and its chemical neutrality to water effect allows implement the idea of catalysis of water hydrolysis process. Graphene is susceptible to modifications and to affecting its physico-chemical properties (creation of materials for construction of organic electrodes, photovoltaic cells or construction of layers of solar collectors).

Fig. 1. Structure of graphene.



Source: http://naukawpolsce.pap.pl

Some words about sorption capabilities....

Carbon-based materials may absorb well the particles of, *inter alia*, H_2. The results of physical sorption, conducted with graphene, have indicated its very high affinity to absorption of the hydrogen molecules and, what is most important (in storage aspect) owing to the mechanical tensions, the control of gas release from graphene is possible[4] [3]. Looking at these problems, it seems therefore, to be the ideal material, increasing the possibilities of energy storage in a form of hydrogen, isn't it so?

The above fact was developed, *inter alia*, by the research team of the University of Technology of Łódź, working upon the graphene tank, allowing riding about 800 km without the necessity of refuelling the car (hydrogen as a fuel[5]) [3]. The process of absorption and recovery of particles was performed on the principle of the change in temperatures, with the consideration of the earlier mentioned property of graphene to control the sorption-desorption cycles. The searches for methodology and materials for the increase and improvement of the currently obtained results in respect of the quantity as well as quality of the hydrogen in the reverse gas storehouses is a priority in the discussed sector of pro-hydrogen policy.

Lack of the sufficient hydrogen infrastructure

Unfortunately, the development of hydrogen infrastructure is slow. It is inhibited by a lack of the need (that is, still too low demand) and the prices of hydrogen for final users are highly dependent on the number of refuelling (let's imagine such situation at petrol station!?) Are there the stations which sell as much hydrogen per day as it is delivered? The total length of hydrogen

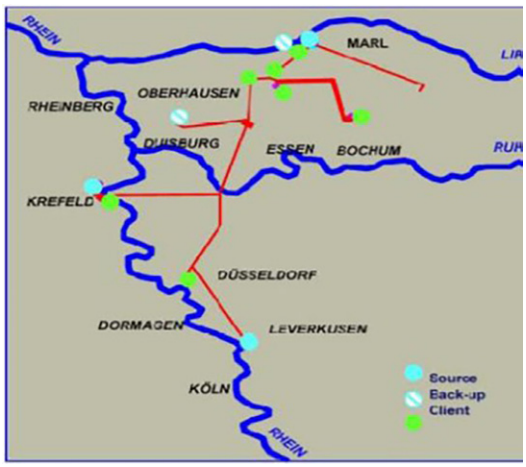
[3] „Institute of Car Transport (ITS) has prepared the plan of the project for construction a network of several stations in Poland where it would be possible to fuel the vehicles (buses and personal cars) powered by fuel links, with hydrogen. ITS is one of the institutions, implementing the European Project Hit-2-Corridors, the aim of which is to create and later on, integrate with the European infrastructural network, serving for utilization of hydrogen as fuel in road transport" – Wojciech Gis explains. One of the effects of the work on the discussed project includes plan of building the stations in Poland, mainly in the courses of the European transport corridors TEN-T. The answer to the question: "when it will be possible?" is not easy. The Institute assumes the establishment of such 9 object up to 2030, depending on the interest. "http://www.pb.pl/4365094,94750,polska-bedzie-miala-stacje-wodorowe?utm_source=copyPaste&utm_medium=referral&utm_campaign=Firefox (access 2015/12/03)

[4] The document „Graphene is a new material base on carbon", developed by Agnieszka Jedrzejczak, Multi-person post for foreign economic cooperation and entrepreneurship, as placed in portal http://www.mazovia.pl, presenting the possibilities for graphene applications in aspect of its physical and chemical properties. Separation of functions of hydrogen and aspect of its storage

[5] Vision of Prof. Piotr Kula, director of the Institute of Material Engineering of the University of Technology of Łódź, based upon the so-far obtained results of the studies on the application of graphene in the motorization revolution. The interview by Jack Krywko for wyborcza.pl

pipelines in Europe is ca. 1500 km. It is a very effective way of energy transportation – the losses in the hydrogen transfer are at least by twice lower than those ones occurring in the transfer of energy by transfer lines. The gas pipelines are constructed from a special steel (hydrogen supplants carbon) with diameter of 25–30 cm and allow hydrogen pumping under the pressure of 10–20 bar. The oldest hydrogen network in Europe is found in the Ruhr area where the 50 years old gas pipeline has a length of 210 km and joins 18 suppliers and recipients without any failure. The oldest line (400 km) combines the plants in France and Belgium.

Fig. 2. The system of hydrogen gas pipelines in the Ruhr area (acc. to Air Liquide www.airLiquide.com 2005).

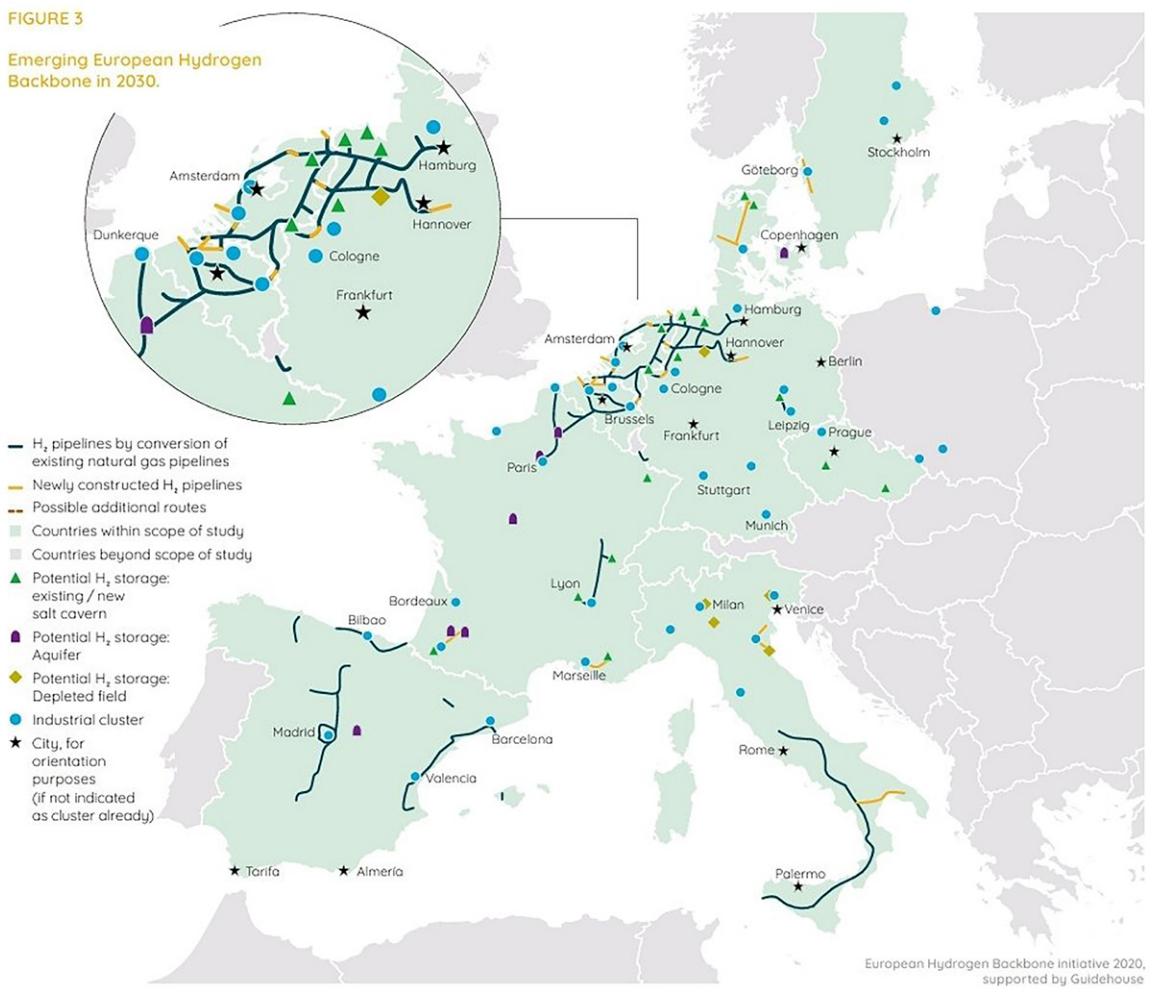


The key problem before the researchers is the application of cavern technologies for storage of hydrogen as energy and performance of salt caverns, meeting the safety requirements in respect of leak-tightness and stability. We know to-day that they should be situated in the regions, enabling utilization of brine coming from leaching and receipt of energy to the network of high tensions. The storing installations of hydrogen should be located in the vicinity of potential sites of its utilization.

In July 2020, the report entitled "European Hydrogen Backbone" [4] sponsored by some operators of transmission systems (Enagás, Energinet, Fluxys Belgium, Gasunie, GRTgaz, NET4GAS, OGE, ONTRAS, Snam, Swedegas, Teréga) was published. In the mentioned document, the transmission network for hydrogen in Europe was preliminarily outlined.

In the document [4], the analysis included 10 European countries (in our region, only the Czech Republic). The main thesis of the Report is the opinion that on the grounds of the existing network or *via* the so-called "upgrade", the change of the existing non-used gas pipelines, it would be possible to speak about creating the beginnings for the hydrogen backbone of Europe as early as in 2025, in the perspective of 2030. The starting point should be the hydrogen network, existing in France, the Netherlands and its development in Germany.

Fig. 3. The European planned hydrogen infrastructure. The European hydrogen backbone. Source: EUROPEAN HYDROGEN BACKBONE. Anthony Wang, Kees van der Leun, Daan peters, Maud Buseman [4] .



As it is given by the International Energy Agency (IEA), hydrogen at the global scale, in the contrary to Europe, is almost completely obtained from natural gas and carbon [5] (production of the so-called synthesis gas); water hydrolysis is considerably more expensive and requires distillation. Its production – ca. 70 million t annually in a pure form – the further 45 million t without previous separation – is responsible for the total CO_2 emission, estimated at 830 million t.

Then, IEA informs that there are huge regional differences in the costs of hydrogen production. Natural gas without CCUS (Carbon Capture, Utilization and Storage) is at present the most economic source of hydrogen production in majority of the world, at such low costs as e.g. 1 USD/kg H_2 in the Middle East region. From among the low-emission options, electrolysis requires price of electric energy at 10-40 USD /MWh to become competitive in respect of costs for natural gas from CCUS technology (depending on local gas prices). In the available literature, we may find information that the cost of producing 1 kg H_2 from fossil fuels, connected with CO_2 emission to atmosphere is about 1.5 €. For comparison, the cost of production of 1 kg of H_2 from fossil fuels in combination with sequestration of CO_2 is equal to almost 2.0 €[2]. In such situation, the plans of the European Commission concerning promotion of building and development of renewable – green hydrogen market, the costs of which are estimated depending on the price of electric energy at 2.5 – 5.5 €/kg[6], are somewhat puzzling.

At the turn of May and June 2020, the road map was passed on to social consultations; the mentioned map was aimed at obtaining the social contribution to the EU hydrogen strategy under development. In the mentioned document, the chances and challenges before the development of trans-border market of "green" hydrogen in the EU were generally described. The mentioned document is consistent with the policy of obtaining a climatic neutrality of Europe until 2050:

- its main aims include lack of net emission of greenhouse gases to atmosphere and bringing about the separation of the economic growth and resources. The role of hydrogen in the assumptions of this ambitious climate policy cannot be overestimated. Hydrogen is expected to replace, first of all, fossil fuels in those sectors where cannot be fully electrified and allow storing the electric energy, generated from RES (renewable energy sources) during the period of excessive production. The purpose of the consultations was to submit the information on barriers and challenges which – in the opinion of the social side – do not allow creating the profitable and competitive market of hydrogen in Europe in short and long term perspective.
- they concerned the complete life cycle of "green" hydrogen, commencing from the stage of creating the legal framework and unification of nomenclature, problems connected with the wide production and integration with electric network, transmission and storage of hydrogen, ending on the requirements connected with the necessity of adapting the equipment of final users, indispensable development of new hydrogen technologies and the necessity to ensure the appropriate financial means and the suggestions for the terms of their granting.

Within the frames of the cited work [6] the obtained comments were analysed in the context of the challenges, standing before the European chemical industry, being connected with the plans for decarbonisation.

Analysis of the conclusions in the context of the countries of origin and size of the enterprises

The opinions on the road map were reported in the period of 26 May – 08 June 2020. In total, 279 remarks from 24 countries were submitted. In our opinion, the time came to utilize a potential of hydrogen. At present, hydrogen is mainly used in crude oil refining and in production of ammonia, i.e. further of artificial fertilizers; it occurs in trace amounts in transport. If the discussed universal element is to have a significant contribution to clean energy and become a bridge of energetic transformation, we have to find a place for it in the sectors where it is almost absent. It must be found in everyday life areas such as human life, transport, buildings and energy production. For this to happen, a modern technology of its effective obtaining is necessary. (Humanity has not known yet such technology, not only the cheap one. It would be fantastic if the discussed process could run as exergonic reaction requiring less energy than that one which would be obtained later when combusting hydrogen). Hydrogen is the universal element; it may be comprehensively employed. As early as two years ago, we wrote about methane hydrates [7]. It is a very interesting source of hydrogen; the question, however, arises: will we be successful in this undertaking? Whether the humanity will open new horizons? Perhaps a new Copernicus or a new Maxwell[7] will discover the new successive evidences?

In the past, the false starts for hydrogen technology had place; our time is to be different. "*In this century, we will subdue the power of the stars, the source of the energy of Gods. In a short time perspective, it means introduction of era of solar-hydrogen energy which would replace fossil fuels, and in a longer perspective, it means mastering nuclear fusion and even solar energy from the space.*" [2].

Hydrogen must begin to play a key role as a cheap, clean, safe fuel of the energy of the future. Hydrogen may help in solving different critical energy problems. Hydrogen must begin to play the main role in energetic transformation of humanity as:

- It will release a high-scale integration of RES with the so-far energy producers,
- It is the easy energy storehouse,
- It is a buffer of energetic safety,

[6] The European Commission, A hydrogen strategy for climate-neutral Europe. COM (2020) 301 final, 8.7. 2020, Brussels https://ec.europa.eu/energy/sites/ener/files/hydrogen_strategy [access on line: 14.09.2020]

[7] Maxwell proved that electricity and magnetism ate two kinds of the same phenomenon - electromagnetism. He demonstrated also that electric field and magnetic field disperse in a vacuum with the speed of light in a form of wave, i.e. light is electromagnetic wave.

- It is a clean raw material for the industry.

There is a will to have such micro-market in Poland. It seems that PKN Orlen is a leader in this respect; the enterprise specifies it quite clearly: If the fuel companies want - in the future - to exist in the market, they have to consider with what to replace oil and petrol in petrol stations. The company wants to develop also capacities of hydrogen production in electrolysis process and, also, the infrastructure for charging the vehicles, driven in Poland. It's the beginning. If we want to exist in the market as a fuel company, we must take into consideration that the mentioned oil and petroleum in the fuel stations should be replaced with something. They will contain also chargers of electric cars as they have to be. Personally, I cannot see the batteries-driven electric cars. I am more convinced to electric vehicles, driven by hydrogen. Hydrogen-driven car is the electric car. Hydrogen is not combusted. It is transformed in fuel cell and generates current. It is exactly the same what electric car but it does not possess battery but hydrogen cell. The difference between such vehicles is visible especially in the respect of their distance. In the case of hydrogen-driven Toyota cars it is 500–700 km. As far as heavy transport is concerned, i.e. buses and trucks, the battery is not an option because it would occupy a half of the truck's surface in order to pass 1000–1200 km. It could be ensured by hydrogen. In Poland, the hydrogen stations do not exist yet, but PKN Orlen wants to develop such objects in Poland[8)].

The preferred green hydrogen in the strategy of Germany

Utilization of hydrogen in order to decarbonise the economy requires, however, obtaining it in the way which does not generate emissions. At present, the discussed raw material, used mainly in the refinery and chemical industries, is generated almost exclusively in the processes of steam reforming of natural gas or carbon re-gasification. The both mentioned methods are connected with CO_2 emission, therefore, the generated product is specified as grey hydrogen. On the other hand, electrolysis is emission-non-generating process; it requires water and electric energy from renewable sources. Green hydrogen, obtained by this way, is considered as the only one solution, which meets the needs of the sustainable development in a long perspective. Another method for hydrogen production, which is considered in the context of decarbonisation of the economy, includes its obtaining from natural gas, with the utilization of technology of CO_2 sequestration (CCS, *carbon capture and storage*), that is, the process consisting in the capture of CO_2 from exhaust fumes in order to store it e.g. in salt caverns or under the sea bottom. Blue hydrogen, as obtained by this method, is treated, however, for example in Germany, as only a transitional solution. Due to a wide availability of natural gas and lower costs of such raw material as compared to the green hydrogen, a partial decision on blue hydrogen may accelerate the process of establishing hydrogen economy. This option gives also a chance to the companies from gas sector for the adaptation to the needs of decarbonisation. Contrary to the green hydrogen, its blue equivalent is not the emission-free product because during the production and transportation of natural gas, harmful methane is released to atmosphere.

Strategy for green hydrogen in France

In September 2020, the Ministers Barbara Pompili and Bruno le Maire submitted the report on the state of the national strategy in respect of green hydrogen to the main French entities and companies, associated in the Hydrogen and Fuel Cell Association connected with the hydrogen economy. Within the frames of restructuring plan, France Relance Covid, the French Government plans to obtain 6.5 GW power in the installation for hydrogen production up to 2030. Within the frames of France reliance, 7.2 billion € will be destined for hydrogen strategy until 2030, including 2 billion € up to 2020. The French Government has defined three priorities concerning hydrogen. First one includes decarbonisation of industry, with the application of hydrogen coming from electrolysis and not from fossil fuels. According to the mentioned aim, France will commence the project concerning hydrogen in the field of sustainable production of batteries. It refers, in particular, to the projects of electrolysers with power of gigawatts. The second priority is utilization of hydrogen as a fuel in public transport, in delivery vehicles and trains. This year, the auction of 350 million € value for innovative project in the discussed area, is anticipated. Also, the project of purchase of "innovative big-scale objects of industrial ecosystem" of 275 million € is also planned. In 2021, the Government will destine 65 million € for the third priority connected with hydrogen, i.e. program of the research and development in the research institutes, universities and engineering schools. 3.4 million € assigned to hydrogen up to 2023 will be divided in a following way: 54% for decarbonisation, 27% for public transport and services and 19% for research and development, innovations and training.

Poland and hydrogen

The work upon the national strategy for development of hydrogen economy is conducted at the Inter-ministerial Governmental Team for Hydrogen Management with the participation of the Ministry of Climate. The Team works on the coherent vision of developing hydrogen utilization not only as a raw material and fuel but also as energy carrier which may be additionally stored. The hydrogen perspective should be a natural consequence, recorded in the Energetic Policy of Poland up to 2040. The mentioned document is again amended and – as we understand – subjected to comprehensive social consultations; it has not been adopted as the binding document, by the Government of the Republic of Poland. From the

[8)] Józef Węgrecki, the member of the board for operating matters of PKN Orlen during the 5th Polish Economic Summit, held in Siedlce

perspective of the authors, acting, for many years, in the domain of comprehensively understood energetics, the basic problem to be settled is a stable – cross-party – economic policy from which a clear, long-term energetic policy is resulting, without opportunism and meanness. In this context, we should mention still unsettled problem of obtaining land for linear investments, i.e. the draft law on strategic investments of public aim. We are for a quick development of hydrogen technologies.

The Team "*wants to strive at independence on the specified technological solutions, all this will be implemented with the assumption that the mentioned neutrality would not generate costs which might exceed the potential advantages coming from its reaching*". *Probably, it would be not possible in all domains; we will be striving at its obtaining in the places where there is a chance. We witnessed several times the situation where the dependence on a defined technology or on the supplier of such technology implied huge costs in a short time period. Therefore, obtaining the appropriate efficiency in green hydrogen production is the important aim but in the perspective of Polish hydrogen development, we take grey hydrogen also into account. It would create the foundation of hydrogen economy which then, owing to energy excesses from renewable source, will be supplemented with the electrolysers and completely zero-emission hydrogen. The hydrogenization as the element of energetic transformation must include also local, Polish specificity. The mentioned transformation must be the responsible process which would allow not only changing the picture of our energetics but also would contribute to development of Poland, ensuring a new economic dynamics and new work places to the local communities.*

Generation of the effect of inter-sector synergy is the element necessary for further effective work on the development of hydrogen sector in our country. The particular market tycoons may get much; however, the maximum advantages coming from development of hydrogen technologies in Poland is possible only with the assumption of possessing comprehensive know-how and resources, including energetic and fuel sectors. Such approach results from the nature of the discussed technologies and the potential of their later utilization. Therefore, the transformations in the mentioned above sectors are the answer to the needs generated by the market. We expect that they will give the appropriate stimulus to the Polish hydrogen sector and will bring advantages coming from synergy.

A private sector has also a significant role to play. It is already now involved in the link of values of hydrogen economy. A lot of the private companies develop successively the solutions in favour of hydrogen purification, storage and transport. There are also interested in commencement of producing hydrogen from RES [...].

We should also mention multi-level cooperation not only between the ministries, on public-private or even cross-nation level but also between the government and self-governing organs. The units of territorial self-governing authorities as being close to local market possess the most precise knowledge about the local needs and potential. Therefore, they will be able to direct the governmental support and indicate the appropriate investments. The cooperation at this level may obtain a form of financing the purchase of hydrogen –driven buses or in the support of building the heat power plants, based on the hydrogen technologies; they would constitute the effective source of heat and, at the same time, would have a great influence on the improvement of the air quality.

What foreign partners are taken into consideration?

We are open to any possibilities and solutions. We perceive a foreign cooperation as cooperation at the EU forum. We look also at the countries outside the Community and the non-governmental organizations which utilize developed hydrogen engineering. We plan to base the cooperation on four pillars: exchange of technology and experience, elaboration of common European and international standards in the field of hydrogen technologies, active participation in developing the EU regulations and finally, financing of hydrogen transformation in the European Union. As far as the EU is concerned, we look especially at our main commercial partners who- similarly as Poland- perceive a considerable potential in hydrogen. Simultaneously, we are open to any possibility of cooperation. In the non-European scale, we count first of all, on the countries, rich in the acquired experience in this respect, i.e. Japan, Australia and the South Korea. We do not exclude also the cooperation with our American allies."

What should the hydrogen strategy contain – the key assumptions

Global consumption of gas (certainly), oil (probably) and carbon (probably) will be still increasing in absolute values for the next two decades, even gradually with the increase of the share of renewable energy sources in the energy market. Taking the above fact into consideration, probably there is no way for reaching the global aims in respect of CO_2 emission and global increase in temperature which is not connected with a considerable increase of the electric energy production from nuclear and water energy.

Further combustion of big quantities of fossil fuels will have to be connected with a wide introduction of modern low-emission technologies in order to equalize the supposed increase of the emission; together with the development of renewable energy sources and other source of energy, oil and gas will follow carbon and will be forced, more and more frequently, to compete in prices with other sources as to maintain their role in the energetic mix.

Carbon preserved its high role in energetic system in the second half of the 20th century and at the beginning of the 21st c., as being, unfortunately, cheaper than its alternatives.

Oil and gas will follow, probably, by the same way. Together with the development of alternatives such as renewable energy sources, oil and gas will have to remain relatively cheap to maintain their markets.

The future changes in prices will accelerate the passage to competitive energy sources and will cause a loss of the to-

day levels in energetic mix. In particular, the consumption of oil will be more and more forced to the competition between the sources, when considering the possible higher prices and costs of CO_2 emissions.

Position of OPEC will have to evolve from the current attempt to maximize the incomes via limitation of production and increasing the prices for protection of its participation in the market. In the second half of the twenties and in the thirties of the 21st century, OPEC will be more occupied with the allocation of production and investing in new, not completely developed sectors and itself will probably be suffering from chronic surplus of manufacturing capacities; a cheap source of grey hydrogen will appear which – without regulations – will be effectively supplant and delay the development of green hydrogen technology.

Summing up

I would like to cite Prof. Konrad Świrski: "Unfortunately, it seems that to-day in Poland there are no possibilities of reasonable "social agreement" and compromised solution of the problem. Everything is going, unfortunately, towards a serious economic and social problem – perhaps one of the greatest problems during the recent 30 years. The successive directives and resolutions of the European Parliament will be pressing on quicker departure from carbon (during the coming days, even increase of the aim of emission reduction up to 2030 to 50–55% or even 60% is expected) what would be slowly unattainable technically for Poland, not speaking about economic costs. The attempt of strong restructuring of mining industry, being a consequence of energetic transformations (as in the new PEP 2040) will be stopped by resistance of the current carbon sector what , in consequence, will lead to dramatic discrepancy between the European and Polish policy (and the problem with the cost of emissions which will be quickly increasing in Europe). A real change will occur, alas, not as a result of "social mini-agreement" but in the period of a strong economic crisis which perhaps may occur in our country in the coming 10 years and automatically, it will force closure of the coal mines. As it usually happens in the history of the world, certain processes are unavoidable and unfortunately, the interests of individuals always fall in confrontation with the new changes in technology[9].

The international energetic-climatic policy forces us to seek for the alternative solutions and sources of cheap electric energy. The aspects of storage and transmission of hydrogen on the industrial scale and optimization of the process of its obtaining (production) seem to be the priorities. We know what hydrogen is, we know its properties we are able to collect and transform it into electric energy. The ideas of its storage are dynamically developing.

We hope that after the lecture of this paper, the Reader will have a question: when the "outburst of the hydrogen era" will take place. In our opinion, the mentioned period was commenced in the second decade of the 21st century. Hundreds of articles concerning the possibilities of utilizing hydrogen-driven mechanical vehicles, planned hydrogen refuelling stations, or construction of underground storehouses for H_2 in salt caverns are the premise of this trend. Perhaps it is enough that some would lie down under the apple tree or enter the tub with water and cry: "Eureka"!! (The motto for today is: to introduce graphene revolution and RES into the era of hydrogen!).

Economic aspects in such approach include optimization of manufacturing processes, storage and transmission of hydrogen in the industrial scale. The key may be the so-called wax foundation – the "leaven" of chemical honey plaster – Graphene.

And perhaps the future belongs to sorbents with a high capacity! And perhaps the future will be completely different?

References

Internet pages and portals www:

[1] http://www.pb.pl/4365094,94750,polska-bedzie-miala-stacje-wodorowe?utm_source=copyPaste&utm_medium=referral&utm_campaign=Firefox (dostęp 2015/12/03)
[2] http://www.mazovia.pl „Grafen to nowy materiał na bazie węgla" Oprac. Agnieszka Jędrzejczak
[3] http://m.wyborcza.pl/wyborcza/1,105407,14699355,Naukowcy_z_Lodzi_zrobia_rewolucje_w_motoryzacji_.html Wizja prof. Piotrem Kuli, dyrektora Instytutu Inżynierii Materiałowej Politechniki Łódzkiej, oparta na dotychczas uzyskanych wynikach badań nad zastosowaniem grafenu w zrewolucjonizowaniu motoryzacji. Wywiad przeprowadzony przez Jacka Krywko dla wyborcza.pl
[4] http://swiat.pl/aktualnosci/grafen-m-obnizyc-koszty-pozyskiwania-wodoru-z--dla-fcevs_385.html Ewa Buczyńska „Grafen może obniżyć koszty pozyskiwania wodoru z dla FCEVs" opublikowany na portalu swiat.pl
[5] http://www.itechpost.com/articles/10154/20130604/new-catalyst-fuel-cells-made-graphene-help-boost-renewable-energy.htm Artykuł autorstwa James Maynard „New catalyst for fuel cells made from graphene could help boost renewable energy, e-cars"
[6] http://www.sciencedaily.com/releases/2013/06/130605111518.htm Artykuł „Metal-free catalyst outperforms platinum in fuel cell" opublikowany na portalu sciencedaily.com 5.czerwca.2013
[7] http://www.bateriegrafenowe.pl/katoda-lfp-poprawiona-za-pomoca-grafenu
[8] http://spectrum.ieee.org/nanoclast/semiconductors/materials/3d-hybrid-supercapacitor-made-with-graphene/
[9] http://biznes.pl/swiat/superkondensator-z-grafenowego-zelu/6l4hg
[10] http://gramwzielone.pl/energia-sloneczna/8999/grafen-nadzieja-dla-fotowoltaiki „Grafen nadzieją dla fotowoltaiki?" opublikowany na portaly gramwzielone.pl
[11] http://grupaazoty.com/
[12] http://www.kierunekchemia.pl
[13] http://inwestor.lotos.pl
[14] http://cleantechnica.com
[15] http://naukawpolsce.pap.pl/
[16] http://evertiq.pl/
[17] portal energetyka.wnp.pl

[9] https://www.cire.pl/item,204185,13.htlm?utm_source=newslatter&utm_campaign=newsletter&utm_medium=link&apu=21600

[18] https://www.ech2a.eu/ informacja dot. Europejskiego sojuszu na rzecz czystego wodoru.

Papers and publications:

[19] Sikora A., „Wodór budulec Wszechświata, ziemska anomalia, czy powszechnie dostępne paliwo?" Chemia Przemysłowa 6/2019(743) ISSN 1734-8013 p. 38-41.

[20] Klima K., Sikora A., „Wszechobecny. Mamy wodór i co dalej...?" Energetyka Cieplna i Zawodowa 2/2016 (628) Str. 48-49. ISSN 1734-7823

[21] Klima K., Sikora A., „Zamknięta w wodorze. Mamy wodór i co dalej...?" cz.2 Energetyka Cieplna i Zawodowa 3/2016 (634) p. 108-113. ISSN 1734-7823

[23] EUROPEAN HYDROGEN BACKBONE.; Anthony Wang, Kees van der Leun, Daan Peters, Maud Buseman

[24] The Future of Hydrogen. Report prepared by the IEA for the G20, Japan www.iea.com lipiec 2019.

[25] Biały R., Potempa M., Sikora A., Szurlej A., „Wyzwania stojące przed europejskim przemysłem chemicznym w kontekście unijnej strategii wodorowej." Przemysł Chemiczny 8/2020; vol. 99 p.1101-1105; DOI: 10.15199/62.2020.8.1

[26] Sikora A., Uwięziona" cząsteczka — [Trapped molecule] / Andrzej Paweł SIKORA // Energetyka Cieplna i Zawodowa ; ISSN 1734-7823. — Inne tytuły czasopisma: Branżowy Magazyn Przemysłowy. Energetyka Cieplna i Zawodowa ; BMP Energetyka Cieplna i Zawodowa. — 2014 No. 4, p. 56–57. — Bibliogr. p. 57. — Afiliacja: Akademia Górniczo-Hutnicza

[27] Prof. dr hab. Leszek Czepirski –Technologie magazynowania i oczyszczania wodoru dla energetyki przyszłości

[28] Case Western Reserve University: Metal-free catalyst outperforms platinum in fuel cell. 2013.

Article reviewed
Received: 19.10.2020 r./Accepted: 30.11.2020 r.

PKN ORLEN
WILL BUILD A HYDROGEN HUB IN WŁOCŁAWEK

By the end of 2021, PKN ORLEN will construct hydrogen hub in Włocławek which will be able to produce up to 600 kg of purified hydrogen per hour. The mentioned investment will include the installation, producing hydrogen of the quality corresponding to the quality of transport fuel, the logistic infrastructure and also, fuelling stations. In the first stage of distribution, the fuel will be destined, first of all, for public and commodity transport. The concern has already signed some agreements with the self-governing organs, being the potential user of hydrogen.

"We are perfectly aware of the challenges connected with the global trend of a new mobility; therefore, our strategy assumes also a successive development of alternative fuels and low-emission technologies. We are convinced that in the future, hydrogen will be a very important fuel, utilized in transport; so, we intensify work in this area. Our aim is to strengthen the position of leader in this requiring market. The investment which will be implemented as early as in the next year in Włocławek, is a milestone enabling the effective competition with the greatest players in our region. In the next step, we plan to implement a similar hub in PKN ORLEN refinery in Płock. The installation for purification of hydrogen is also generated in our bio-refinery in Trzebinia – says **Daniel Obajtek, the President of the Board of PKN ORLEN**.

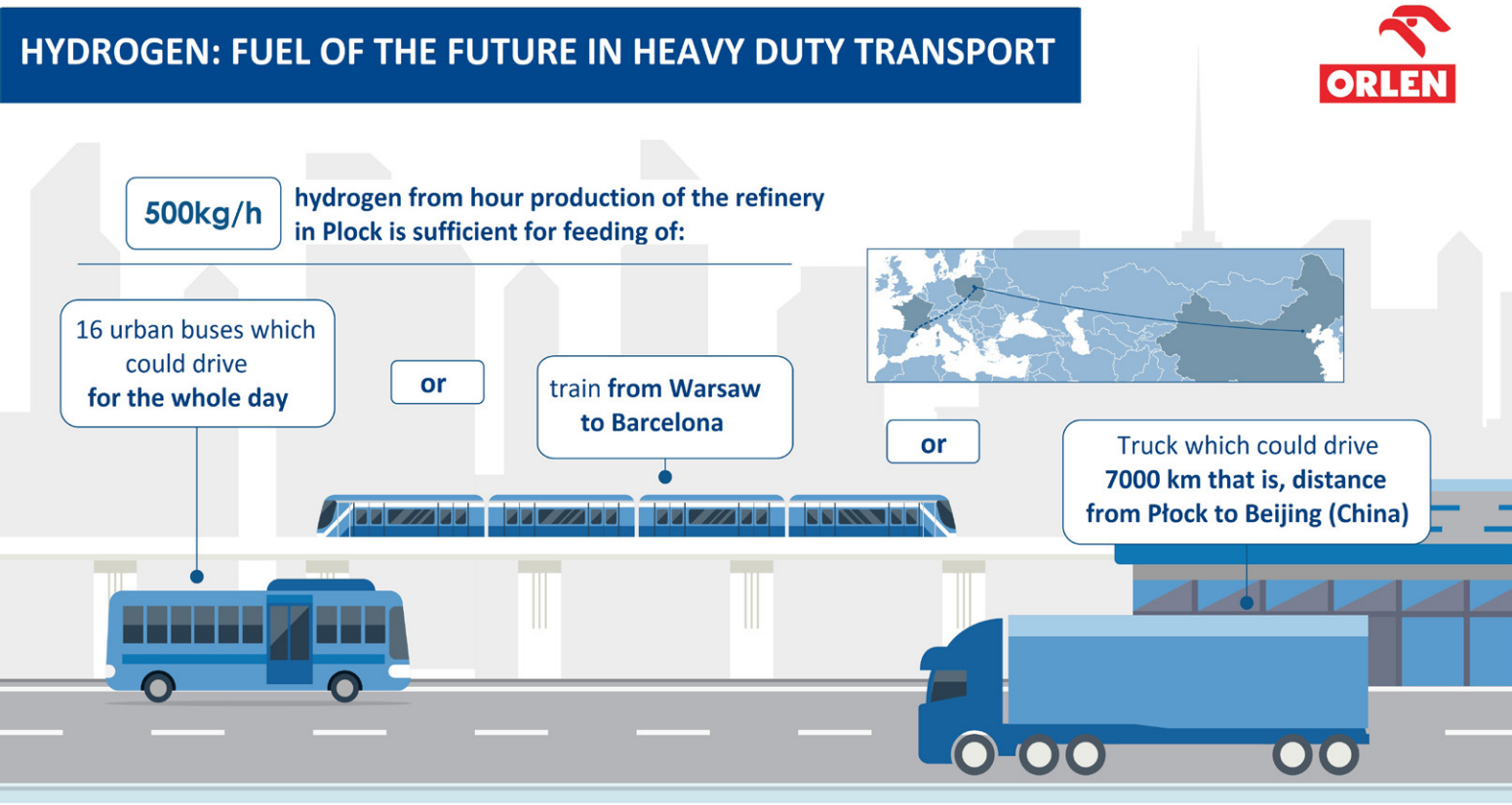
Hydrogen hub in Włocławek will be situated at the territory of ANWIL plant. At the first stage, the manufacturing capacities of the installation will amount to ca. 170 kg/h, however, its modular construction will allow elastic increasing of production together with the increase of demand. Hydrogen, as being purified in Włocławek, is generated in the environment-friendly process of brine electrolysis as a by-product of the process of obtaining chlorine and until now it was utilized in the ammonia producing installations. The method of purification of hydrogen is presently the subject of analyses carried out together with the technical advisor for the mentioned investment. The implemented project will consist of installation for hydrogen purification, infrastructure of fuel loading on the trucks and cisterns, transport semitrailers, system of hydrogen fuel supply and two refuelling stations.

Hydrogen purified in Włoclawek, at the first stage of distribution, will be destined, first of all, for public and commodity transport, including the rail one. The concern has already signed the letters of intention concerning cooperation in favour of development of public hydrogen-operated transport, with Górnośląsk-Zagłębiowska Metropoly, Cracow Communal Holding and Urban Transport Enterprise in Cracow and with Płock. The agreements concluded with the successive self-governing authorities are under run. The Concern has also signed a letter of intention with PESA Bydgoszcz for construction of hydrogen-operated locomotive, which will be used for logistic needs of PKN ORLEN.

Together with the development of market, hydrogen fuel will get to the personal cars and long-distance buses. In longer perspective, the Concern assumes deliveries of hydrogen for the needs of ships, ferries, or stationary applications such as heating etc. There is also planned the possibility of selling hydrogen to the third entities which will introduce it to other outlets, e.g. food or metallurgical industry. Apart from hydrogen hub in Włocławek and the similar investment planned in Plock, PKN ORLEN develops also hydrogen technologies in bio-refinery ORLEN Południe in Trzebinia. The commencement of hydrogen production of the transport fuel quality is planned there in 2021.

The drivers of personal cars may already refuel hydrogen in two stations of ORLEN Group in Germany, whereas in June 2021, such possibility will appear also in three fuel stations in the Czech Republic.

„Network of hydrogen public transport affects actually the return of the investing costs, born on the refuelling stations and supports the budding but possessing-the-potential individual hydrogen transport which is also the area of strategic investments of PKN ORLEN. Especially, at the first stage of hydrogen technology development, it will have the greatest meaning in public and commodity transport. Therefore, we undertake the cooperation with the self-governing authorities as well as with the transport companies; it will enable occupying a strong position on the market and, on the other hand, it will give the possibility to develop independently the technology. In the cities of the north and west Europe, the test projects of hydrogen public transport



are developed and low-emission buses become integral element of local public infrastructure. it is a good direction" – stresses **Józef Węgrecki, the member of the Board of PKN ORLEN for operating matters**.

Investment on infrastructure for hydrogen fuel-based transport are in accordance with the European strategy of sustainable development and are the answer to the EU environment targets, assuming that until 2030, transport sector will minimize the emissions of greenhouse gases to atmosphere by 30% as compared to values from 2005. Apart from electro-mobility biofuels of the 2nd generation, hydrogen is listed as a fuel of future, which may actually lead to the implementation of the European environmental aims.

Due to technical and economic reasons, the greatest present potential of hydrogen is perceived in public transport and cargo. Bus with hydrogen drive has a range of ca. 350–450 km and at one refuelling (lasting ca. 10 min.) it may drive for the whole day. In exploitation cycle, estimated at ca. 12 years, the replacement of one urban bus having a diesel engine by hydrogen-operated vehicle may prevent emission of 800 tons of CO_2 to atmosphere. Moreover, the engines of the hydrogen-driven buses are by ca. 20% more silent as compared to the traditional ones.

Source: https://www.orlen.pl/PL/BiuroPrasowe/Strony/PKN-ORLEN-wybuduje-hub-wodorowy-we-W%C5%82oc%C5%82awku.aspx?fbclid=IwAR1dJoboj_8sTVWVDcWg0epschqI8UQ-GdBFBHTdnPfus3N_EYWHteLxZbA

Prepared on the basis of press releases from PKN Orlen
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DOI: 10.15199/180.2020.4.2

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ACHMATOWICZ REARRANGEMENT – 50 YEARS OF APPLICATION

PÓŁ WIEKU ZASTOSOWAŃ PRZEGRUPOWANIA ACHMATOWICZA

MOTTO: TANTUM SCIMUS, QUANTUM MEMORIA TENEMUS.

Summary: *Chemical sciences proved instrumental in formulating theories and in providing materials which are crucial for development of contemporary technical civilization. Methods of chemical synthesis, necessary for supply of materials designed for specific technical needs have attained efficiency, which allows preparation of even most complicated molecules encountered in Nature. Academic stereo- and enantioselective total syntheses of natural products (such as: alkaloids, peptides, isoprenoids, lipids, carbohydrates and phenolics) are generally regarded as the top achievements of XX century organic chemistry. Along the line, this paper recalls ingenious project of total synthesis from simple furan derivatives, of pyranes and pyranosides, basic stuff of natural carbohydrates, suitably functionalized for a stepwise conversion into variety of sugar structures. The project designed in the Institute of Organic Chemistry, Polish Academy of Sciences in Warsaw, began its proof of principle experimental validation in 1970. Its success led to a widespread application of what is presently known as the Achmatowicz reaction/Achmatowicz rearrangement for syntheses of simple and complex, oxygen and nitrogen heterocyclic systems, including great variety of natural products.*

Keywords: *Furylcarbinols, pyrans, pyranoses, monosaccharides, total syntheses of natural and modified sugars, unsaturated sugars, Achmatowicz rearrangement*

Streszczenie: *Nauki chemiczne odegrały kluczową rolę w kształtowaniu zarówno podstaw teoretycznych jak i zaplecza materialnego współczesnej cywilizacji przemysłowej. Metody syntezy chemicznej, niezbędne do wytwarzania materiałów technicznych o pożądanych właściwościach, osiągnęły sprawność pozwalającą na otrzymanie związków odpowiadających cząsteczkom organicznym pochodzenia biologicznego, o najwyższym stopniu złożoności. Syntezy totalne, stereo- i enancjoselektywne, związków naturalnych (alkaloidów, peptydów, izoprenoidów, lipidów, węglowodanów i związków fenolowych) uznano za najważniejsze osiągnięcia klasycznej chemii organicznej. Poniżej przedstawiamy genezę i rozwój projektu totalnej syntezy z prostych pochodnych furanu, wielofunkcyjnych piranów i piranoz – zasadniczej heterocyklicznej sześcioczłonowej struktury pierścieniowej naturalnych cukrów, glikozydów i ich oligomerycznych pochodnych, opracowanego w Instytucie Chemii Organicznej PAN w Warszawie, który w 1970-tym roku osiągnął zrealizowaną z powodzeniem fazę weryfikacji doświadczalnej. Osiągnięcie, które zyskało nazwę reakcji (przegrupowania) Achmatowicza, stanowi obecnie jedno z popularniejszych narzędzi stereokontrolowanej syntezy tlenowych i azotowych związków heterocyklicznych.*

Słowa kluczowe: *furylokarbinole, pirany, piranozy, monosacharydy, totalne syntezy cukrów prostych, nienasycone piranozy, przegrupowanie Achmatowicza*

Introduction

There is a relatively well established opinion in academia, shared by larger learned circles, that chemical sciences in Poland are well developed and scientific achievements of contemporary Polish scientists are properly recognized in the global scientific literature [1]. From the organic chemistry standpoint, the perception of towering achievements in the last century have been focused on total organic syntheses of natural products (NP), particularly secondary metabolites (SM), in their versions allowing for the efficient control of the target's chirality. Secondary metabolites, which exhibit a wide diversity of selective biological activities, became indispensable as lead compounds and therapeutic agents for contemporary medicine and pharmaceutical industry. They are very seldom available from natural sources in quantities required for industrial manufacturing of pharmaceutical active substances and their preparations, hence the continuous interest in their alternative resources. Chemical synthesis, which started in XIXth century from targeting as simple chemical molecules as urea (F. Wöhler, 1828) and acetic acid (H. Kolbe, 1845), quickly expanded its scope to thousands of reactions and millions of various products of increased complexity. It has become a new reliable source of useful natural products and their analogs and mimics for structure – activity relationship studies. Total syntheses of complex, multifunctional, polycyclic and loaded with chiral centers natural products, such as: alkaloids, antibiotics, vitamins, isoprenoids and acetogenins, has throughout the last century served as the ultimate test of chemists ingenuity in planning and craft in executing of multistep sequences of

Osman Achmatowicz (Born Dec. 20 1931, Vilnius) – Professor of organic chemistry in research and education institutions in Warsaw since 1975, active researcher and educator in natural products chemistry, structure elucidation, stereoselective synthesis, and organic stereochemistry. Member of the IUPAC committees (1978-2017), Polish Chemical Society (Deputy President [1982-1986], awarded Kostanecki Medal 1983), Society for Advancement and Propagation of Science, Societas Scientiarum Varsoviensis and other. Fellow of the World Innovation Foundation since 2002. Son of Professor Osman Achmatowicz (1899-1988), also distinguished organic chemist.
O. Achmatowicz graduated from Chemistry Department Warsaw Technical University in 1955. Obtained his Ph. D. (1961) and D. Sc. (1967) from University of Warsaw. Visiting Scientist of: National Research Council of Canada (1961-1963), University of California San Francisco (1963-1964), Queens University, Kingston, Ont., Canada (1973-1974) and Wisconsin University, Madison, WI, USA (1986-1987).

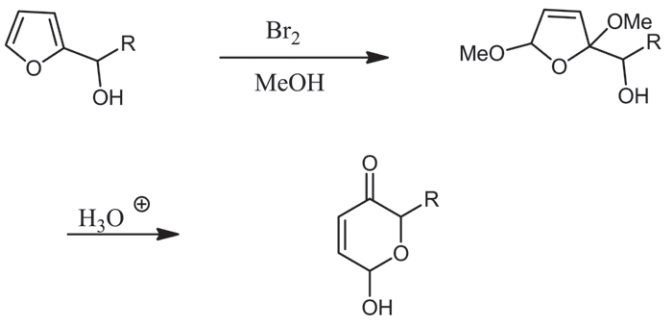
Osman Achmatowicz (ur. 20 grudnia 1931 w Wilnie) – Profesor chemii organicznej, kolejno w IChO PAN (1975-1977), SGGW (1977-1991) i w Instytucie Farmaceutycznym (1991-2012). Specjalizował się w chemii związków naturalnych (alkaloidy, antybiotyki, węglowodany), stereochemii, organicznej syntezie enancjoselektywnej; jest ekspertem w dziedzinie nomenklatury chemicznej. Syn Osmana Achmatowicza (1899-1988) także chemika organika. Autor reakcji imiennej o szerokim zastosowaniu w syntezie i chemii związków naturalnych. Absolwent Wydziału Chemicznego Politechniki Warszawskiej (1955), stopień naukowy doktora uzyskał w 1961 roku a habilitację w 1967 roku na Wydziale Chemii Uniwersytetu Warszawskiego. Tytuł naukowy profesora otrzymał w 1975 roku. Wiceprezes ZG PTChem (1982-1986) i Towarzystwa Naukowego Warszawskiego (2001-2004), członek Komisji Nomenklatury Organicznej IUPAC (1978-2011). Działa w Towarzystwie Krzewienia i Popierania Nauk oraz Komisji do spraw Etyki w Nauce PAN. Odbywał staże stypendialne w: National Research Council of Canada w Ottawie (1961–1963), Uniwersytecie Kalifornijskim w San Francisco (1963–1964), Queen's University w Kanadzie (1973–1974). Zajmował także stanowisko profesora wizytującego na Uniwersytecie Wisconsin-Madison w latach 1986–1987. W latach 1991-2011 był sekretarzem Centralnej Komisji do Spraw Stopni i Tytułów Naukowych.

reactions. Simply forming final products was not sufficient; the synthetic steps should be regio- and stereoselective offering as high efficiency of the final outcome as possible [2–6]. Chemistry has attained almost magical power in assembling complex molecules (also with designable functionality), through accumulated knowledge created by generations of exceptionally gifted individual scientists. Sometimes, the accomplishments have been honored by associating the name with a particular molecular transformation or chemical process [7]. Among the recent achievements developed in local academic environment, which enjoy very wide international recognition, we have chosen to single out the Achmatowicz rearrangement (Scheme 1). It is mainly for sentimental reasons, since we were members of the research group which contributed to the general method of total synthesis of carbohydrates, heralded by a seminal publication which appeared in *Tetrahedron* nearly 50 years ago [8]. In the late 1960-ties Aleksander Zamojski and Osman Achmatowicz, the scientists employed by the Institute of Organic Chemistry, Polish Academy of Sciences (IChO, PAS) in Warsaw, conceived a project, aimed at total synthesis of monosaccharides. The two scientists proposed parallel lines of research:

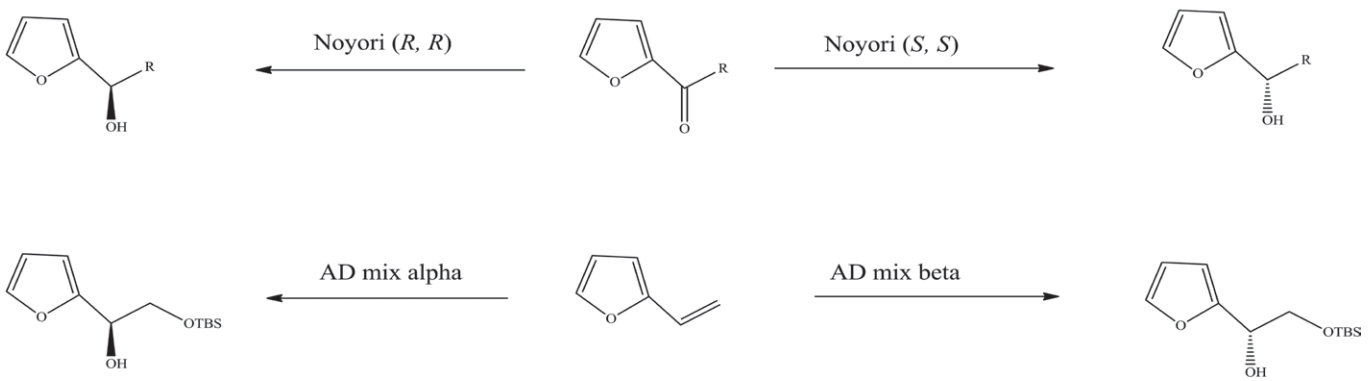
a) an assembly of pyran compounds (monosaccharides) starting from key substrates deriving from the hetero- Diels-Alder reaction;
b) an assembly of pyran compounds starting from the key substrates, relatively easily available methoxylated furan derivatives (formal 1,4-dicarbonyl synthons).

Both total syntheses allowed for an introduction of all functionalities needed to produce a variety of natural pyranosides in a diastereoselective manner. Ultimately, both approaches manned by gifted Ph. D. students proved successful and attracted attention of wide circles of natural product chemistry researchers. This paper is devoted to some reminiscences of the Achmatowicz rearrangement (ARE) (Scheme 1) [7, 8], origins and its extraordinary dynamic development as the furan pathway to carbohydrates, and its follow up applications in wider perspective of natural product synthesis. Scheme of canonical version of the transformation reported in 1971 as the general approach to monosaccharides is presented below. (R = H, CH_3, CH_2OH).

Scheme 1. A stepwise transformation of furyl carbinols into pyranose enuloses, versatile synthons for natural products, known as Achmatowicz reaction (or Achmatowicz rearrangement)

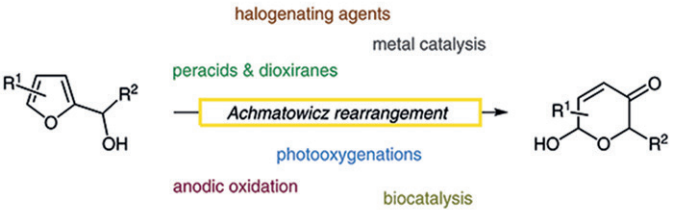


Scheme 2. Access to furylcarbinols of defined chirality from 2-alkylfurylketones and 2-vinylfuran by catalytic reduction (Noyori) and dihydroxylation (Sharpless) procedures



Most 2-furyl alcohols applicable as reactants are chiral. Thus, since the original invention much effort has been invested in securing access to required 2-furyl alcohols of suitable enantiomeric purity (Scheme 2) [9, 10] and developing more efficient transformations. It resulted in a gradual improvements in the stereoselectivity control, atom economy, chemical waste reduction [11–14], switch from stoichiometric to catalytic reagents [15, 16], as well as experimental application and practical deployment of biocatalysis [17, 18] in selective one step reaction depicted on Scheme 2 and 3 below.

Scheme 3. Scope of reagents and conditions driving Achmatowicz rearrangement as a selective single step reaction

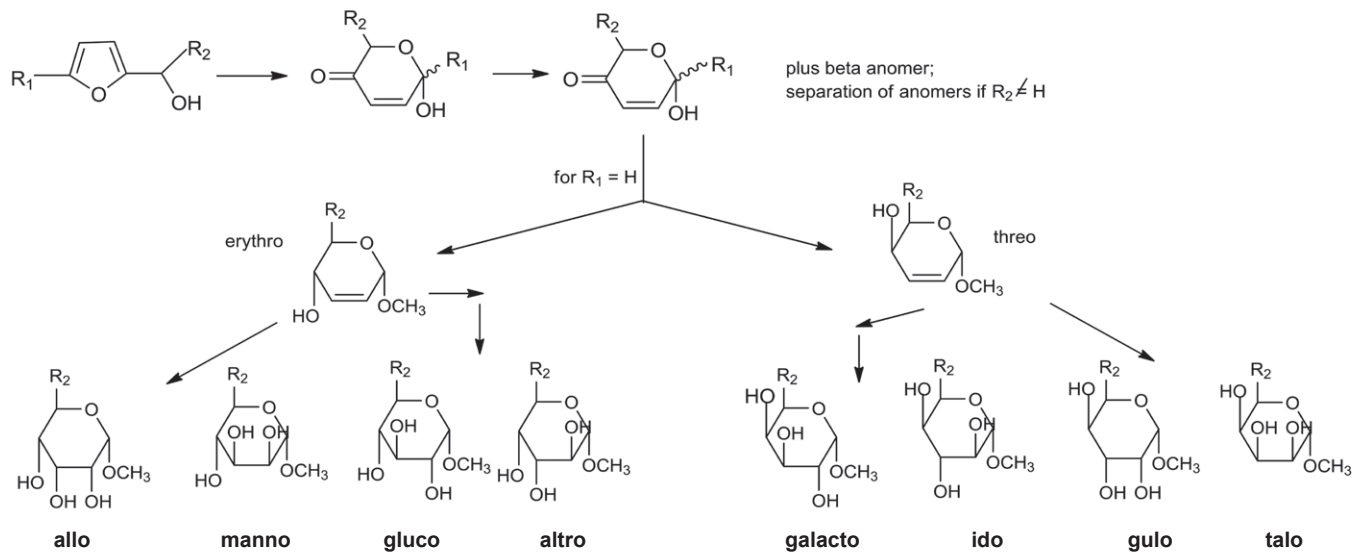


Total syntheses of carbohydrates

Sugars are essential components of a primary as well as secondary metabolism. Generated by carbon dioxide fixation in a multistep electron transfer process summarized as photosynthesis, carried out by green plants equipped with chlorophyll as the catalyst, carbohydrate materials (cellulose, lignans, starch and other polysaccharides) are amassed in agrotechnical crops and natural biomass in quantities exceeding 350 gigatons of carbon dioxide turnover per annum globally. Yet, apart from a few common sugars qualifying as commodity chemicals (cellulose, glucose, sucrose, lactose, etc.), many mono- and oligosaccharides are in short supply as raw materials for particular purposes such as pharmaceutical manufacturing, biotechnology, bioengineering and synthetic biology [19,20]. Glycans, glycoproteins, glycolipids and other glycoconjugates are of utmost importance to most biological functions and processes registered as normal physiology or markers of pathology. Consequently, various sugar molecules, from monosaccharide analogs and simple glycosides to complex branched chain oligosaccharides, are employed as therapeutics with functions spanning from enzyme inhibitors to vaccines [21, 22]. Early knowledge of carbohydrate structure frequently represented by molecular formula $C_n(H_2O)_n$ inspired attempts like formaldehyde condensation under moderate basic conditions (Butlerov reaction), which indeed has produced a sweet tasting mixture of sugar like substances, called formose. Remarkably, Emil Fischer managed to prove unanimously around 1900 that formose contains grape sugar – glucose, albeit in racemic form. Fischer's studies on sugars and their synthetic derivatives culminated in the first total synthesis of D-glucose, during which configuration of four consecutive chiral centers was properly assembled [23]. Throughout XX century, the numerous attempts were made to design and develop various practical approaches to syntheses of carbohydrates from non-sugar substrates, and vast literature of these efforts is discussed in comprehensive reviews [24–28]. The approach conceived by O. Achmatowicz around 1970 was based on a well-established conversion of furan compounds into 2,5-dialkoxy-2,5-dihydro derivatives, electrochemically, or under bromine catalysis; such compounds were by then already used as 1,4-dicarbonyl synthon precursors for assembly of various heterocyclic systems [11, 15, 16].

Ingenious plan of the stepwise conversion of suitably functionalized furan derivatives into naturally occurring pyranoses begins with alfa 2-furylcarbinols. They were to be exposed to dialkoxylation followed by a mild acidic hydrolysis. This treatment should bring about a spontaneous rearrangement into 2,3-unsaturated-pyranose-4-ulose, a pyran derivative (Scheme 1) suitably functionalized for subsequent stepwise transformations into regular or structurally modified monosaccharides [8]. Thus, 2-furylcarbinol was considered a suitable precursor of

Scheme 4. General scheme illustrating the Achmatowicz approach to monosaccharides (R = H for aldopentoses, R = CH_3 for 6-deoxyaldohexoses, and R = CH_2OH for aldohexoses

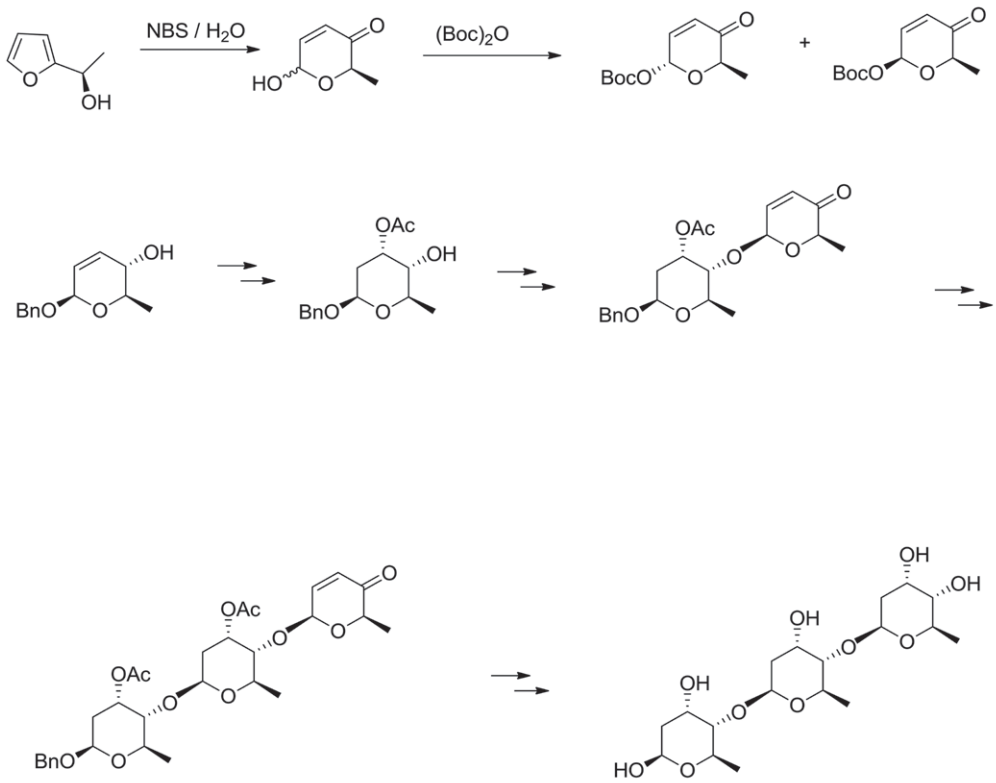


pentopyranoses, while 2-furylethanol should provide precursor for 6-deoxyhexoses, and 2-furylethanediol, for natural hexoses. The power of the outlined concept resides in multifunctionality of the key enulose intermediate and a possibility of an excellent diastereoselectivity control in a sequence of planned reactions, like carbonyl group reduction, followed by the double bond conversion into a *cis*- or *trans*- vicinal diols, through dihydroxylation or epoxidation followed by hydrolysis. The plan of synthesis is presented in a following scheme which shows the robustness of the methodology allowing synthesizing practically any monosaccharide [8]

It should be stressed, that although above scheme represent syntheses of pentoses or hexoses as racemic mixtures, it was realized from the beginning that the alfa-furyl carbinol carbon atom, if chirally substituted, should preserve its configuration throughout the rearrangement, and therefore the method should be applicable to synthesis of monosaccharides of either D- or L-series (subject to availability of furylcarbinols of suitable absolute configuration). That working hypothesis was successfully verified by synthesis of methyl glycosides of selected D- and L-aldohexoses [29, 30] after meticulous preparations of (S-)- and (R+)- furylcarbinols by classic separation of their diastereomeric derivatives. The main part of the project was concluded in approximately four years with completing of five Ph. D. Theses, defended in the IChO, PAS in Warsaw, by P. Bukowski, B. Szechner, R. Bielski, Z. Zwierzchowska and H.M. Burzyńska, under the supervision of Professor O. Achmatowicz. In summary, the following classes of monosaccharides have been obtained as methyl glycosides: aldopentopyranoses [31, 32], deoxyhexoses of antibiotic origin (aculose, amicetose, cinerulose and 6-deoxyaldohexoses; [33–35]), regular aldohexoses [36] and ketopentopyranoses and ketohexopyranoseses [37–38]. Some additional syntheses were completed within Achmatowicz's group, apart from the ongoing Ph. D. program. These included: ribose derivatives [39], noviose [40], 6-deoxy-6-nitro-mannose [41], antibiotic aminohexose glycosides – kanosaminide [30] and aminooctose - lincosaminide [42]. Racemic pentenulose was also tested, in form of anomeric esters, as glycosylation synthon for preparation of O- and C- glycosides under Lewis acid catalysis [43, 44]. Finally, the same racemic synthon was used for syntheses of disaccharide precursors from suitably protected D-monosaccharides, demonstrating facile chromatographic separation of obtained diastereoisomeric mixtures [45, 46]. The results summarized in referenced publications and the recent book chapters [47, 48] have proven the soundness of the initial concept, and have demonstrated its practical experimental viability; in principle, all exercised chemical transformations secured facile every step diastereoisomer resolution, for both operational purposes - analytical control (TLC; HPLC) and preparative separation (SiO_2 column chromatography).

When many years later O'Doherty published an extensive review on asymmetric synthesis of sugars in Advances in Carbohydrate Chemistry and Biochemistry [28] substantial portion of the chapter was devoted to application of the Achmatowicz rearrangement. In retrospect, it can be concluded that the appreciation of the rearrangement applicability was rather slow at first, but exploded when availability of chiral furyl carbinols was secured by facile asymmetric hydrogenation of 2-furyl ketones with use of Noyori catalysts or via Sharpless dihydroxylation of 2-vinylfuran (Scheme 2) [9, 10]. Vinylfuran,

Scheme 5. The key steps of digitoxose synthesis, trisaccharide sugar moiety which constitutes a glucon part of cardiotonic Digitalis glycosides [49, 50]



which can be easily generated from furfural, by using methylenating or hydroxymethylenating C1 synthons like Wittig or Grignard reagents, can also be converted to useful vicinal hydroxyaminated synthons. It is worth adding that synthetic, enantiomerically pure enuloses, like D-aculose, have gained great popularity as O- and C- glycosylating synthons in Pd catalyzed preparative protocols, particularly useful for glycodiversification, in oligosaccharide synthesis [49–51], and preparation of natural glycosides and glycoconjugates [28, 52, 53]. They have been also applied in syntheses of other natural products, including acetogenin antibiotics, terpenoid saponins, and alkaloids [28, 54-57].

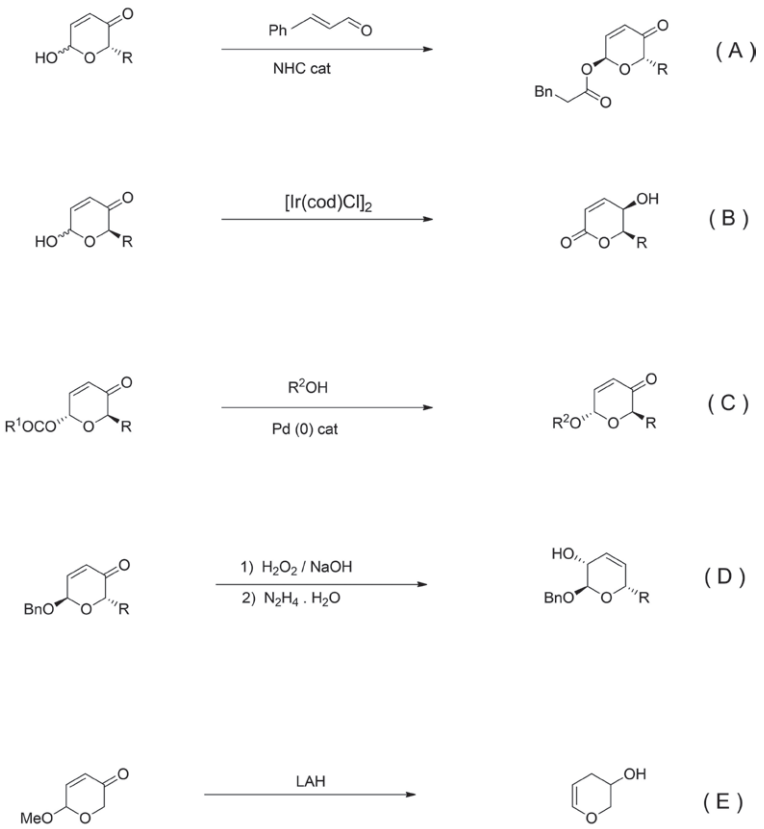
Short outline of pyranosuloses chemistry

Primary ARE products (Scheme 1) were named pyran-2-en-4-osuloses by the rearrangement originators, who preferred sugar nomenclature, and/or 6-hydroxy-2H-pyran-2(3H)-ones by some other authors. They were also referred to as „enuloses" or „lactols" in short, to stress the presence of a hemiacetal center, essential for further transformations. These small molecules, already resembling some natural pyranoses, are heavily loaded in functionality. In a conjugated double bond containing pyrane ring every carbon atom represents some diverse but selective reactivity, which can be applied for chemical derivatization and/or introduction of additional functional groups [8] as illustrated on Schemes 6 and 7. Evidently, the most important issue in a pyranosulose further functionalization, is stereoselectivity. It has been repeatedly demonstrated that the substrate furylcarbinol carbon atom preserves its configuration throughout the rearrangement but to enforce further chirality control and integrity additional means have to be devised. Anomeric mixture formation can easily be avoided in case of hexoses or higher sugars by constructing 1,6-anhydro bicyclic ring system, which ensures an excellent diastereoselection [58, 59]. Pentenuloses or 6-deoxyhexenuloses can be conveniently transformed into optically active compounds by constructing chiral molybdenum and iridium complexes, which can be separated by column chromatography into air-stable pro-D and pro-L monosaccharide precursors [60–62]. Additionally, iridium catalyzed dynamic kinetic isomerization can convert 2,3-en-4-uloses into regioisomeric unsaturated lactones with excellent control of newly created C-4 chiral center. (Scheme 6 B)

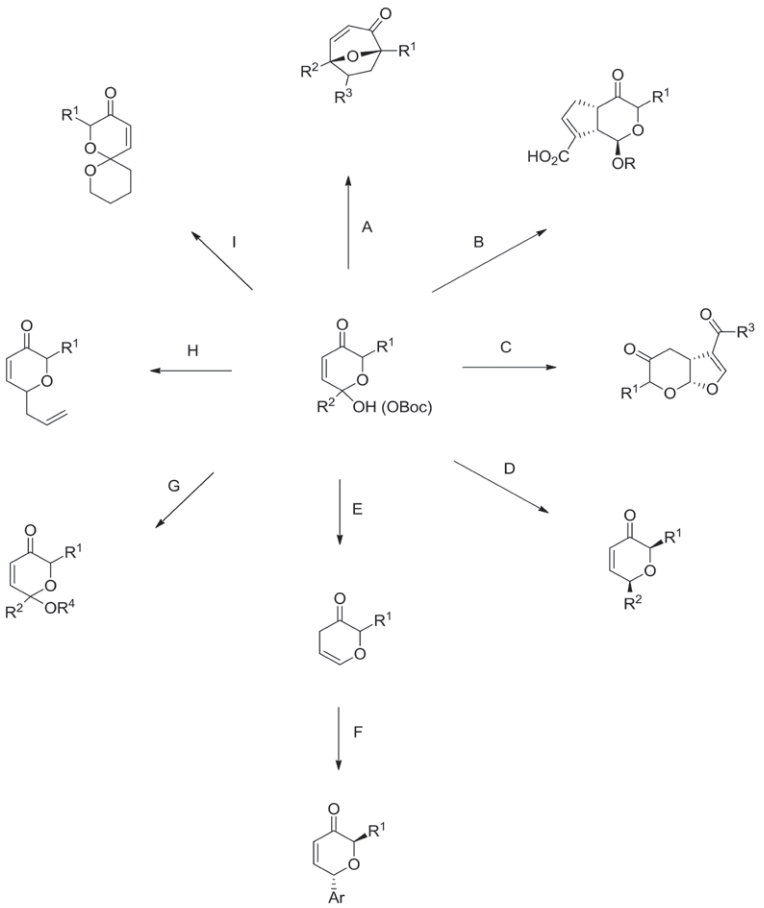
Double bond reactivity is rather typical, featuring formation of Michael products on exposition to carbanion precursors [63–65] (but also known in aza- and oxa-Michael versions), photochemically activated C-C bond formation in reaction with isopropanol, and Diels-Alder cycloadditions even with non-activated substrates like butadiene. Enulose esters can be selectively acylated under kinetically or thermodynamically controlled conditions. It can be also accomplished by N-heterocyclic carbene catalyzed dynamic kinetic resolution or organometallic enantiomeric scaffolds, which afford very efficient glycosyl donors for Pd (0) catalyzed reactions with alcohol, saccharide, or phenol acceptors [66–69]. It has been established that anomeric Boc (*t*-butylcarboxy) substituent is particularly useful for such glycosylations, in which configuration of the anomeric center is retained [52, 53]. With such a wide array of stereocontrolled glycosylation methods (occasionally called etherification) ARE synthons become easily manageable and competitive sugar precursors, applicable in syntheses of complex targets, instead of natural sugars pool, which involves inevitable multistep protection-deprotection sequences and typical difficulties at the glycosylation step. Use of enuloses as glycosyl donors offers wide opportunities for glycodiversification in medicinal chemistry, as demonstrated in preparation of new analogs of cardiac glycosides and antibiotic sugars [50, 51]. Potential of enuloses anomeric exchange is undoubtedly more extensive than O-glycosylation, as exemplified by facile C-arylation carried out on ARE product esters, with arylboronic acids [76]. Obviously, enuloses and their glycosides can undergo plethora of known 1,2- , 1,4- and 3,4 addition reactions, typical for conjugated enone sytems, like double bond saturation, ketone reduction, Michael addition, etc. [56, 65, 70]. In particular, attaining some feasibility of the 2,3-double bond relocation, via Wharton rearrangement or reductive transformation of 2,3-enulosides [70–72] makes more room for stereocontrolled anomeric center chemistry focusing on O- and C- glycosylations [73-78]. (Scheme 7) On the less obvious side of enulose reactivity array are dipolar cycloadditions, made useful through detailed insight in their mechanism and stereoselectivity. ARE products can be made into reagents for a variety of dipolar cycloadditions, facilitating formation of condensed ring systems. These include oxa-[3 + 2] and [5 + 2] cycloadditions [79–81], which pave way to condensed (fused) ring O-heterocyclic products. Transition from carbohydrate-related pyranoses to a large group of naturally occurring pyrans which are typically 2,6-alkylated, is now possible by application of Kishi reductive procedure [82], which applies hydrosilanes in the presence of Lewis acids for stereoselective removal of a hemiacetal hydrogen atom. (Scheme 7) Interestingly, pyranosenuloses can also undergo ring contraction under basic and thermal activation conditions, providing substituted cyclopentenes by a rearrangement resembling Piancatelli reaction of furylcarbinols. That ring contraction reaction found application in the synthesis of some simple antibiotic molecules, like terrein or pentenomycin [99, 100] and remains of potential interest for prostaglandin syntheses. Finally, ARE can be applied as a step in biomass conversion into platform commodity chemicals (like 5 or 6 carbon chain aliphatic alcohols, diols or triols) from furfural or 5-hydroxymethyl furfural – typical sugar dehydration products. In order to illustrate better the potential of ARE, we decided to supplement its short schematic characteristic of Schemes 6 and 7 by a selection of natural product targets, chosen from hundreds of recently published syntheses [83 – 100], (Scheme 8).

If only a single example of the ARE synthetic significance could be selected for presentation out of the large collection amassed in recent decades, a polycyclic marine toxin would

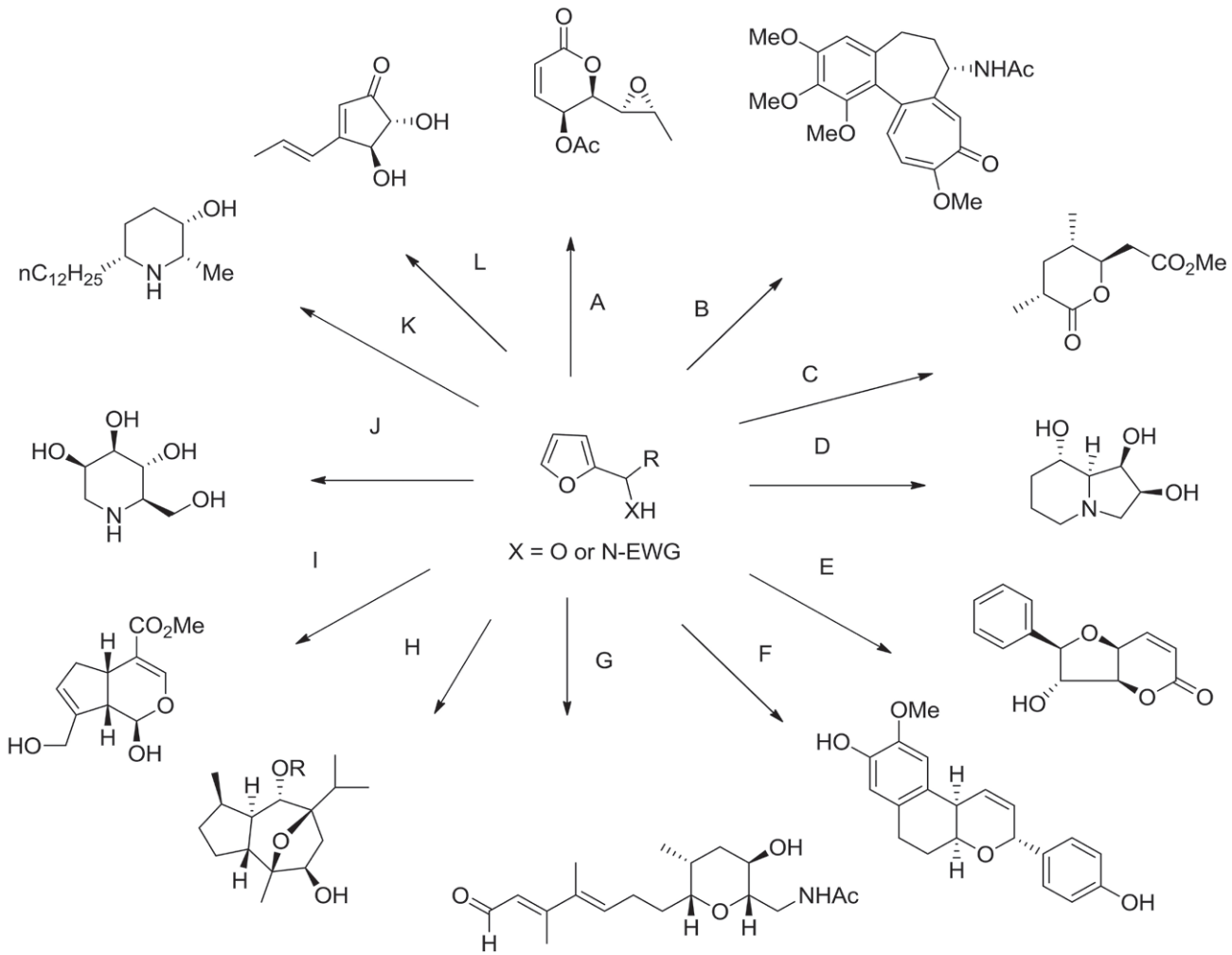
Scheme 6. Examples of the regio- and stereo- selective transformations of ARE hemiacetals, anomeric esters, and glycosides which add versatility to their synthetic potential (Refs. 60-78)



Scheme 7. Selected enulose transformations: A) 5 + 2 cycloaddition; B) 3 + 2 cycloaddition; C) oxa- 3 + 2 cycloaddition; D) Kishi reduction; E,F) for R^2 = H reductive elimination followed by Matsuda-Heck arylation; G) Pd catalyzed glycosylation; H) anomeric C-allylation; I) intramolecular bicycloketalization for R^2 = ω-hydroxybutyl. (Refs.: 65 and 73 – 82)



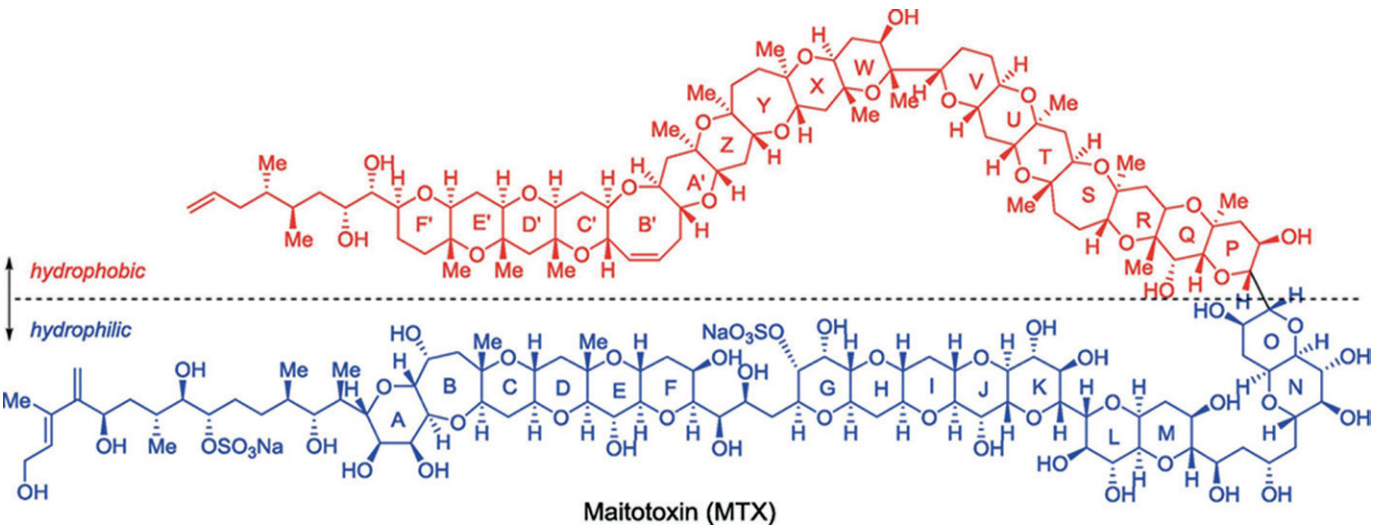
Scheme 8. Examples of the ARE synthetic targets prepared from furylcarbinols or corresponding amine derivatives. The 12 examples shown were selected from hundreds of ARE syntheses described in literature in the last few decades. A) asperlin [83,84]; B) colchicine [85]; C) Prelog-Djerassi lactone [86,87]; D) L-swainsonine [88]; E) isoaltholactone [89]; F) musellarin [90,91]; G) breviccamide [92]; H) engelrin [93,94]; I) genipin [95]; J) nojirimycin [96]; K) deoxycassine [97,98]; L) terrein [99,100].



have been a likely choice. It is because of their utmost structural and stereochemical complication, but also due to their value for medicinal chemistry and clinical pharmacology [101–102].

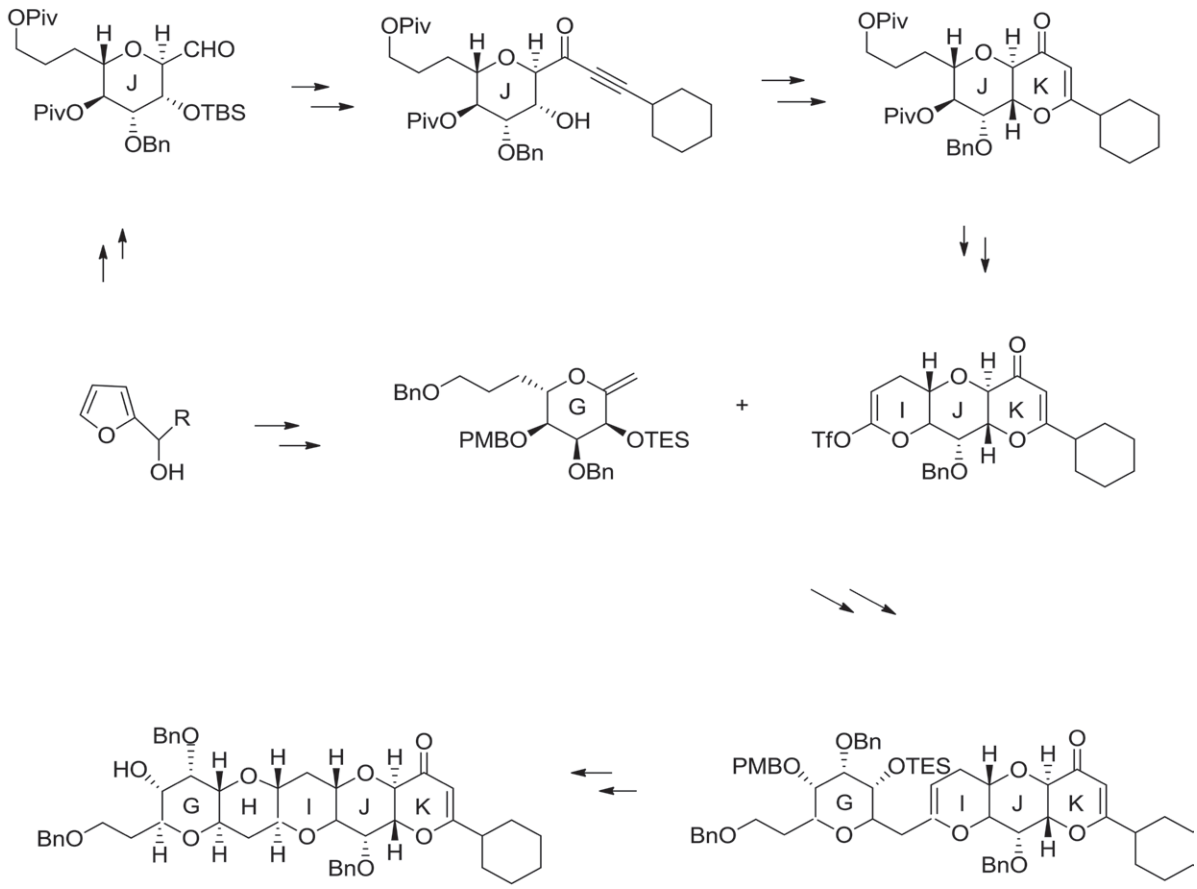
Maitotoxin (MTX), the most complex and the largest non-polymeric secondary metabolite compound ever isolated, is presented in form of 2D formula with graphical indicators of chiral

Scheme 9. Structural formula of maitotoxin



centers configuration. The toxin, isolated in minute amounts from dinoflagellate organism *Gambierdiscus toxicus*, has molecular formula $C_{164}H_{256}O_{68}S_2Na_2$, corresponding to the molecular weight of 3422 Daltons; its molecule is assembled in 32 rings system, which contains 98 chiral centers. Its toxicity against small rodents is phenomenal – LD_{50} ca. 50 ng/kg upon intraperitoneal injection and its connection with calcium channels conductivity is now well established. Availability of MTX and similar marine neurotoxins, responsible for occasional massive poisoning following sea food consumption is extremely low and the substance supply for necessary research depends critically on synthetic capability. It became apparent that elaboration of synthetic methods for preparation of polycyclic ethers of such complexity will involve new methodologies based on stepwise assembly of subunits, based on chiral pyran synthons. Modular approach to MTX polycyclic scaffolds, studied in leading academic organic synthetic centers met with spectacular success relatively recently [103]. Remarkably, an extensive application of ARE chemistry took place in early synthetic stages of several multicyclic MTX domains [104, 105]. An example of GHIJK domain was selected for presenting the key intermediate structures of the multistep synthesis (Scheme 10).

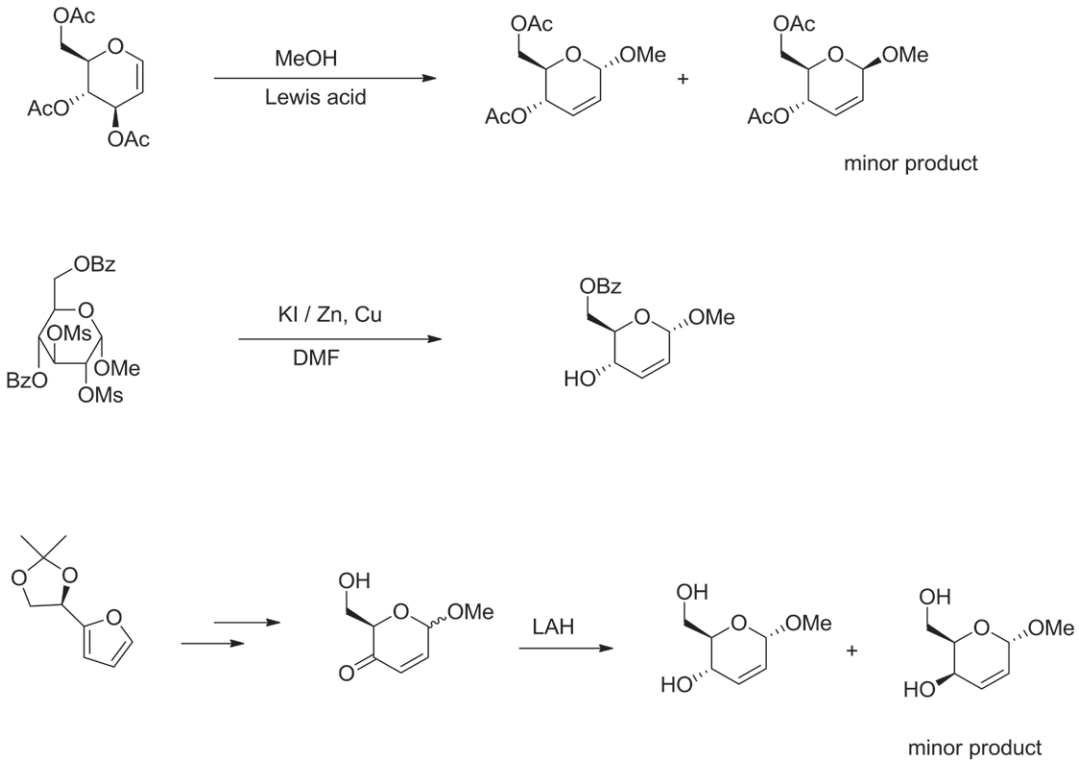
Scheme 10. The key steps in the assembly of GHIJK domain of maitotoxin with deployment of ARE.



Unsaturated sugars between chemistry and biology

Unprecedented advances in general chemical synthesis took place during 20th century. It is despite traditional divisions between relatively narrowly specialized and fragmented fields of interest, e.g. carbohydrate chemists exercised their craft a way apart from chemists interested in oxygen heterocyclic chemistry. The present common perception of organic chemistry as a toolbox for bioinformatics and systems biology, concentrates on effectiveness of synthesis as the way to deliver required compounds, with no reflection on historical distinctions, for which ARE can serve as an illustrious example. While recognized as an efficient method for preparation of multifunctional pyrans and pyranoses during 1970-ties, the rearrangement procedures have been constantly improved. Parallel to significant advancement in research on furan oxidation methods [11, 106], even **well established** ARE procedures [9, 16] are further modified in search for more green and user friendly conditions. Presently, even one pot sequential realization of the ARE initiated reactions under practically anhydrous conditions are achievable [107, 108]. In face of current availability of the ARE synthons and widespread knowledge of their versatility (Schemes 6, 7) it can be concluded that the rearrangement has already merged the mainstream unsaturated carbohydrate chemistry [109-116], once divided between "glycal chemistry" (two upper rows) and "furan chemistry" (lower row) as depicted on Scheme 11.

Scheme 11. Access to 2,3-unsaturated pyranosides from D-glucal triacetate, D-glucoside 2,3-methanosulphonyl-4,6-dibenzoate, and 2-furylethandiol-1,2 derivative. [110,111]



Currently, there is a rich selection of commercially available synthons and efficient methods for their desymmetrization and/or functionalization. Therefore, a judicious choice of planned synthetic pathway should be based on search of the literature of the subject, since even very similar (isomeric) starting materials may require radically different approach. For example, a useful bicyclic synthon, levoglucosenone, is easily obtainable by a single step pyrolysis of cellulose, 1–6 linked D-glucose polymer. The transformation of levoglucosenone to its regioisomer, isolevoglucosenone, requires several steps. However, isolevoglucosenone can be easily prepared from 2-furylethanediol with use of ARE, in two steps [58, 59, 117]. It has been demonstrated on numerous examples, that hex-2,3-enopyranoses obtained by ARE total synthetic procedures from furan substrates can serve as very convenient glycosylation reagents for preparation of oligosaccharides, such as glycons in cardiac glycosides [28,50,51], anthrax toxins [118] and antibiotic sugar moieties [119]. It is very important because corresponding native deoxy-pyranoses are practically unavailable from natural sources. There is already a trend to use these glycosylating synthons for medicinal compounds derivatization and glycodiversification, which is likely to spread to other groups of biologically active compounds [119]. Such translation is feasible because basic synthetic technologies such as enantioselective functionalization of olefins [120], dynamic kinetic transformation of lactols [67, 121] and assorted methods of stereoselective catalytic glycosylations [77, 78] are already in place, and ready to be supported by complementary biocatalytic methods [15–18].

Conclusion

Achmatowicz (and aza-Achmatowicz) rearrangement (ARE) [7], which functions in chemical literature as a name reaction since 1986 [122], was originally described as a general approach to the selective, stepwise synthesis of monosaccharides from simple furan derivatives [8]. Its initial application to preparation of rare sugars, like deoxy and unsaturated pyranoses, as well as racemic and/or D- and L-sugars and their derivatives, were gradually extended to wide selection of pyran and piperidine based natural products and their mimics [47, 56, 57]. The key issue of the total synthetic approach to natural products – chirality control – has been in case of ARE successfully addressed either by an enantioselective chemical catalysis, or biocatalysis [18, 57]. This methodological versatility proven on hundreds of experimental examples, installed ARE as a reliable, validated tool for accessing a variety of oxygen and nitrogen heterocyclic synthetic targets. Particularly strong connection of ARE derived 2, 3-unsaturated pyranoses to biologically active natural products and medicinal chemistry of carbohydrate conjugates has been well documented [47, 57]. Remarkably, ARE which has been continuously improved as far as oxygen delivery and energy transfer for its basic molecular transformation is concerned, fits well into the current trend of postulated transition in synthesis towards green circular chemistry. Thus, after half a century from its commencement, ARE appears to be an active methodological set of validated utility. Evidently, ARE appears to be more than a historical episode since the methodology

goes beyond successful application to challenges of recent decades, and can be easily accommodated to the industry 4.0requirements. In particular, the idea of bio-feedstock as a raw material for furan derived platform chemicals, can adapt ARE as one of the key selective process operations.

References

[1] A.K. Wróblewski, Pozycja nauki polskiej w rankingach międzynarodowych, (2013) Studia BAS, 35: 89–106.
[2] Nicolaou K.C., Sorensen E.J. Classics in Total Synthesis: Targets, Strategies, Methods, Wiley-VCH (1996).
[3] K. C. Nicolaou, E. J. Sorensen, N. Winssinger. (1998) The Art and Science of Organic and Natural Products, J. Chem. Educ. 75:1226-1258.
[4] Nicolaou K.C., Snyder S.A. Classics in Total Synthesis II: More Targets, Strategies, Methods, Wiley-VCH (2003).
[5] Nicolaou K.C., Chen J.S. Classics in Total Synthesis III: Further Targets, Strategies, Methods, Wiley-VCH (2011).
[6] Nicolaou K.C., Hale C.R.H., Nilewski C., Ioannidou H.A. Constructing Molecular Complexity and Diversity: Total Synthesis of Natural Products of Biological and Medicinal Importance, (2012) Chem. Soc. Rev. 41: 5185–5238.
[7] The Comprehensive e-Book of Named Organic Reactions and Their Mechanisms. By Elbertus Kruiswijk. The Chemical Bookstore: Aberaman, U.K. (2005). http://www.namedorganicreactions.co.uk.
[8] O. Achmatowicz Jr., P . Bukowski., B. Szechner, Z. Zwierzchowska, A. Zamojski. Synthesis of methyl 2, 3-dideoxy-DL-alk-2-enopyranosides from furan compounds: A general approach to the total synthesis of monosaccharides, Tetrahedron, (1971), 27:1973-1996.
[9] S.O. Bajaj, R. Farnsworth, G.A. O'Doherty, Enantioselective Synthesis of α- and β- Boc-protected 6-hydroxy-pyranones: Carbohydrate Building Blocks, Org. Synth., (2014), 91:338-355.
[10] X. Yu, G.A. O'Doherty, 1-(2-Furanyl)-1,2-ethanediol, Encyclopedia of Reagents for Organic Synthesis, (2009), https://doi.org/10.1002/047084289X.rn01077, Print ISBN: 9780471936237| Online ISBN: 9780470842898 DOI: 10.1002/047084289X
[11] P. Merino, T. Tejero, J.I. Delsoa, R. Matute, Furan oxidations in organic synthesis: recent advances and applications, Curr. Org. Chem., (2007), 11:1076-1091.
[12] T. Montagnon, D. Kazantzakis, M. Triantafyllakis, M. Stratakis G. Vassilikogiannakis, Furans and singlet oxygen – why there is more to come from this powerful partnership, Chem. Commun., (2014), 50: 15480-15498.
[13] D. Noutsias, I. Alexopoulou, T. Montagnon, G. Vassilikogiannakis, Using water, light, air and spirulina to access a wide variety of polyoxygenatedcompounds, Green Chem., (2012), 14:601-604.
[14] M.J. Palframan, G. Pattenden. The versatility of furfuryl alcohols and furanoxonium ions in synthesis, Chem Commun., (2014), 50:7223-7242
[15] J. Deska, D. Thiel, E. Gianolino, The Achmatowicz rearrangement–oxidative ring expansion of furfuryl alcohols, Synthesis, (2015), 47:3435-3450.
[16] Z. Li, R. Tong, Catalytic, environmentally friendly protocol for Achmatowicz rearrangement, J. Org. Chem., (2016), 81:4847-4855.
[17] F. Blume, P. Sprengart, J. Deska, Lipase-induced oxidative furan rearrangements, Synlett, (2018), 29:1293 – 1296.
[18] D. Thiel, F. Blume, C. Jäger, J. Deska, Chloroperoxidase-catalyzed Achmatowicz rearrangements, Eur. J. Org. Chem. (2018), 2018:2717 – 2725.
[19] Essentials of Glycobiology, 2nd Ed., (A.Varki, R.D. Cummings, J.D. Esko, H.H. Freeze, P. Stanley, C. R. Bertozzi, G.W. Hart, M.E. Etzler. Eds.), Cold Spring Harbor Laboratory Press, New York, 2009
[20] Z. J. Witczak. Carbohydrate Therapeutics: New Developments and Strategies, (2006), Carbohydrate Drug Design, Chapter 2 pp 25-46, ACS Symposium Series Vol. 932
[21] A. Fernandez-Tejada, F.J. Canada, J. Jimenez-Barbero. Recent developments in synthetic carbohydrate-based diagnostics, vaccines, and therapeutics. Chem. Eur. J., (2015), 21: 10616 – 10628.
[22] Carbohydrates in Drug Design and Discovery, (RSC Drug Discovery Series No. 43 ; J. Jimenez-Barbero, F.J. Canada, S. Martin-Santamaria, Eds.) RSC Cambridge UK (2015).
[23] H. Kunz, Emil Fischer – unequalled classicist, master of organic chemistry research, and inspired trailblazer of biological chemistry, Angew. Chem. Int. Ed., (2002), 41:4439-4451.
[24] A. Zamojski, A. Banaszek, G. Grynkiewicz, The synthesis of sugars from non-carbohydrate substrates, Adv. Carbohydr. Chem. Biochem., (1982), 40: 1-129.
[25] T. Hudlicky, D.A. Entwistle, K.K. Pitzer, A.J. Thorpe, Modern methods of monosaccharide synthesis from non-carbohydrate sources, Chem. Rev. (1996), 96:1195-1220.
[26] P. Vogel, I. Robina. De novo synthesis of monosaccharides. In: Glycoscience. Fraser-Reid, B.; Tatsuta, K.; Thiem, J. (Eds.), Springer Verlag Berlin (2008), 857-956.
[27] J. Młynarski, B. Gut, Organocatalytic synthesis of carbohydrates, Chem. Soc. Rev., (2012) 41:587-596.
[28] Aljahdali, A.Z.; Shi, P.; Zhong, Y.; O'Doherty, G.A. De novo asymmetric synthesis of the pyranoses: from monosaccharides to oligosaccharides, Adv. Carbohydr. Chem. Biochem., (2013), 69:55-123.
[29] O. Achmatowicz Jr., R. Bielski, Stereoselective Total synthesis of methyl D- and L- glucopyranosides, Carbohydr. Res., (1977), 55:165-176.
[30] O. Achmatowicz Jr., R. Bielski, Total synthesis of monosaccharides from furan compounds. Synthesis of methyl N-acetyl-2,4,6-tri-O-acetyl-α-L-kanosaminide and methyl α-L-mannopyranoside. Roczniki Chem., (1977); 51:1389-1396.
[31] O. Achmatowicz Jr., P. Bukowski, Reduction of methyl 2,3-dideoxy-DL-pent-2-enopyranosid-4-ulose with sodium borohydride and lithium aluminum hydride, Roczniki Chem., (1973), 47:99-114.
[32] O. Achmatowicz Jr., P. Bukowski, Total synthesis of monosaccharides. Synthesis of methyl DL-pentopyranosides with α- and β- lyxo- , β-ribo- , α-xylo- and α-arabino-configuration, Can. J. Chem., (1975), 53:2524-2530.
[33] O. Achmatowicz Jr., B. Szechner, Total synthesis of racemic 6-deoxyhexoses. Part I. Synthesis of methyl 6-deoxy-α-DL-manno-, β-DL-allo-, α-DL-talo- and α-DL-gulohexopyranosides, Roczniki Chem., (1975), 49:1715-1724.
[34] O. Achmatowicz Jr., B. Szechner, Total synthesis of racemic 6-deoxyhexoses. Part II. Synthesis of methyl 6-deoxy-α-DL-altro, α-DL-gluco- , α-DL-galacto-, and α-DL-idohexopyranosides. Roczniki Chem., (1976), 50:729-736.
[35] O. Achmatowicz Jr., B. Szechner, Total synthesis of racemic methyl 2,3-anhydro-6-deoxyhexopyranosides. Carbohydr. Res., (1976), 50:22-33.
[36] O. Achmatowicz Jr., R. Bielski, P. Bukowski, Total synthesis of monosaccharides. Synthesis of racemic methyl α-manno, α-altro, and β-allo-pyranosides from 1-(2-furyl)-1, 2-dihydroxyethane, Rocz. Chem., (1976), 50:1535-1543.
[37] O. Achmatowicz, M.H. Burzyńska, Stereospecific synthesis of methyl D,L-hex-2-ulopyranosides from furan compounds, Tetrahedron, (1982), 38:3507-3513.
[38] O. Achmatowicz Jr., M.H. Burzyńska, Total synthesis of higher-carbon sugars: synthesis of methyl 3,4,5-tri-O-acetyl-1,7-di-O-benzyl-α-DL-gluco-hept-2-ulopyranoside. Carbohydr. Res., (1985), 141:67-76.
[39] O. Achmatowicz Jr., G. Grynkiewicz, Stereoselective synthesis of 2,3-O-isopropylidene-DL-ribofuranose and methyl DL-ribofuranoside from furfuryl alcohol. Carbohydr. Res., (1977), 54:193-198.

[40] O. Achmatowicz, G. Grynkiewicz, B. Szechner, Stereoselective synthesis of methyl β-D,L-novioside. Tetrahedron, (1976), 32:1051-1054.
[41] O. Achmatowicz Jr., G. Grynkiewicz, An approach to stereoselective syntheses of 6-substituted hexoses. Synthesis of racemic methyl 2,3,4-tri-O-acetyl-6-deoxy-6-nitro and 6-deoxy-6-acetamido-α-mannopyranosides, Rocz. Chem., (1976), 50:719-728.
[42] B. Szechner, O. Achmatowicz, A total synthetic route to enantiomerically pure D- and L-aminooctoses: stereocontrolled synthesis of methyl α-D-lincosaminide, J. Carbohydr. Chem., (1992), 11:401-406.
[43] G. Grynkiewicz, J.W. Krajewski, Z. Urbańczyk-Lipkowska, P. Gluziński, A. Zamojski, O- Versus C- alkylation during reactions of 6-benzyloxy-2H-pyran-3(6H)-one with phenols. Molecular structure of a new benzofuran derivative, Polish J. Chem., (1979), 53:2025-2028.
[44] G. Grynkiewicz, A. Zamojski, Electrophilic substitution of aromatic compounds by unsaturated sugar derivatives. Z. Naturforsch., Sect. B, (1980), 35:1024-1027.
[45] G. Grynkiewicz, A. Zamojski, The Synthesis of 6-Hydroxy-2H-pyran-3(6H)-onyl-hexoses, potential precursors of disaccharides, Synth. Commun., (1978), 8:491-496.
[46] G. Grynkiewicz, Synthesis of some disaccharides containing pent-2-enopyranose residues. Carbohydr. Res., (1980), 80:53-62.
[47] G. Grynkiewicz, Achmatowicz rearrangement derived synthons, and their bio-inspired chemistry, Chapt. 2 In: In Advances in Organic Synthesis; (Atta-ur-Rahman, Ed.; Bentham Science Publishers: Sharjah, UAE), (2018); Vol. 10, pp 41-98.
[48] W. Szeja, G. Grynkiewicz, Syntheses of asymmetrically substituted pyrans of natural origin, In: Natural Products as Source of Molecules with Therapeutic Potential: Research & Development, Challenges and Perspectives; (Filho, V.C., Ed.; Springer: Cham, CH) (2018); pp 233-307.
[49] M. Zhou, G.A. O'Doherty, De novo approach to 2-deoxy-β-glycosides: asymmetric syntheses of digoxose and digitoxin, J. Org. Chem., (2007), 72:2485-2493.
[50] H.-Y.L. Wang, W. Xin, M. Zhou, T. Stueckle, Y. Royanasakul, G.A. O'Doherty, Stereochemical survey of digitoxin monosaccharides, ACS Med. Chem. Lett., (2011), 2:73-78.
[51] H.-Y.L. Wang, Y. Royanasakul, G.A. O'Doherty, Synthesis and evaluation of the α-D-/α-L-rhamnosyl and amicetosyl digitoxygenin oligomers as antitumor agents, ACS Med. Chem. Lett., (2011), 2:264-269.
[52] R.S. Babu, G.A. O'Doherty, A palladium-catalyzed glycosylation reaction: the de novo synthesis of natural and unnatural glycosides, J. Am. Chem. Soc., (2003), 125:12406-12407.
[53] R.S. Babu, Zhou, G.A. O'Doherty, De novo synthesis of oligosaccharides using palladium-catalyzed glycosylation reaction, J. Am. Chem. Soc., (2004), 126:3428-3429.
[54] M.D. Burke, E.M. Berger, S.L. Schreiber, A synthesis strategy yielding skeletally diverse small molecules combinatorially, J. Am. Chem. Soc., (2004) 126:14095-14104.
[55] E.A. Couladouros, A.T. Strongilos, Generation of libraries of pharmacophoric structures with increased complexity and diversity by employing polymorphic scaffolds, Angew. Chem. Int. Ed., (2002), 41:3677-3680.
[56] A.K. Ghosh, M. Brindisi, Achmatowicz reaction and its application in the syntheses of bioactive molecules, RSC Adv., (2016), 6:111564-111598.
[57] P.S. Mahajan, V.T. Humne, S.B. Mhaske, Achmatowicz reaction: a versatile tool in bioactive natural products synthesis, Curr. Org. Chem., (2017), 21:503-545.
[58] T. Taniguchi, K. Nakamura, K. Ogasawara, Non-carbohydrate route to levoglucosenone and its enantiomer employing asymmetricdihydroxylation, Synlett, (1996), 1996:971-972.
[59] T. Taniguchi, K. Nakamura, K. Ogasawara, Back to the sugars: a new enantio- and diastereocontrolled route to hexoses from furfural, Synthesis, (1999), 1999:341-354.
[60] T.C. Coombs, M.D. Lee IV, H. Wong, M. Armstrong, B. Cheng, et al., Practical, scalable, high-throughput approaches to η3-pyranyl and η3-pyridinyl organometallic enantiomeric scaffolds using the Achmatowicz reaction, J. Org. Chem., (2008), 73:882-888.
[61] H.-Y. Wang, K. Yang, S.R. Bennett, S. Guo, W. Tang, Iridium-catalyzed dynamic kinetic isomerization: expedient synthesis of carbohydrates from Achmatowicz rearrangement products, Angew. Chem. Int. Ed., (2015), 54:8756-8759.
[62] Z. Zhu, H.-Y. Wang, C. Simmons, P.-S. Tseng, X. Qiu et al., Iridium-catalyzed dynamic kinetic stereoselective allylic etherification of Achmatowicz rearrangement products, Adv. Synth. Catal., (2018), 360:595-599.
[63] G. Grynkiewicz, O. Achmatowicz, H. Bartoń, Reactivity of 6-methoxy-3,6-dihydro-2H-pyran-3-one in Michael addition, Rocz. Chem., (1977), 51:1663-
[64] J. Knol, J.F.G.A. JansenF. Van Bolhuis, B.L. Feringa, Asymmetric Diels-Alder reactions and Michael type additions with 6 (R) -3' (R) – pantolactone substituted 2H-pyran-3(6H)-one, Tetrahedron Lett., (1991), 5):7465-7468.
[65] N.L. Holder, The chemistry of hexenuloses, Chem. Rev., (1982), 82:287-332.
[66] H.-Y. Wang, K. Yang, D. Yin, C. Liu, D.A. Glazier, W. Tang, Chiral catalyst-directed dynamic kinetic diastereoselective acylation of lactols for de novo synthesis of carbohydrates, Org. Lett., (2015), 17:5272–5275.
[67] C. Zhao, F. Li, J. Wang, N-Heterocyclic carbene catalyzed dynamic kinetic resolution of pyranones, Angew Chem Int Ed., (2016), 55:1820-1824.
[68] S. Yang, X. Fang, Kinetic resolutions enabled by N-heterocyclic carbene catalysis, Curr. Org. Synth., (2017), 14:654-664.
[69] H.-Y. Wang, C.J. Simmons, Y. Zhang, A.M. Smits, P.G. Balzer et al., Chiral catalyst-directed dynamic kinetic diastereoselective acylation of anomeric hydroxyl groups and a controlled reduction of the glycosyl ester products, Org. Lett., (2017), 19:508-511.
[70] M. Cuccarese, H.-Y. L. Wang, G.A. O'Doherty, Application of the Wharton rearrangement for the de novo synthesis of pyranosides with ido, manno, and colito stereochemistry, Eur. J. Org. Chem., (2013), 3067-3075.
[71] O. Achmatowicz Jr., B. Szechner, Tetrahedron Lett., Reductive rearrangement of 2,3-unsaturated methyl pyranosides to 3-deoxy glycals, (1972), 13:1205-1208.
[72] O. Achmatowicz, B. Szechner, Reductive rearrangement of 4-C-substituted hex-2-enopyranosides. Synthesis of 3-deoxy glycals, Tetrahedron Lett., (1997), 38:4701-4704.
[73] Z. Li, R. Tong, Asymmetric total syntheses of the trans-2-aryl-6-alkyltetrahydropyrans Diospongin B and Parvistones D and E from a common precursor, Synthesis, (2016), 48:1630-1636.
[74] S. Tang, Q. Zheng, D.C. Xiong, S. Jiang, Q. Li, X.S. Ye, Stereocontrolled synthesis of 2-deoxy-C-glycopyranosyl arenes using glycals and aromatic amines, Org. Lett., (2018), 20:3079-3082.
[75] F. Otte, B. Schmidt, Matsuda–Heck arylation of glycals for the stereoselective synthesis of aryl C-glycosides, J. Org. Chem., (2019), 84:14816–14829.
[76] M.W. Liaw, W.F. Cheng, R. Tong, C-Aryl glycosylation: palladium-catalyzed aryl–allyl coupling of Achmatowicz rearrangement products with arylboronic acids, J. Org. Chem., (2020), 85:6663-6674.
[77] McKay MJ, Nguyen HM. Recent Advances in Transition Metal-Catalyzed Glycosylation, ACS Catal (2012), 2:1563–1595.
[78] Li X; Zhu J Glycosylation via Transition-Metal Catalysis: Challenges and Opportunities. Eur. J. Org. Chem., (2016), 2016:4724–4767.
[79] H. Pellisier recent developments in the [5 + 2] cycloaddition, Adv. Synth. Catal., (2011), 353:189-218.
[80] K.E.O. Ylijoki, J.M. Stryker, [5 + 2] Cycloaddition reactions in organic and natural product synthesis, Chem. Rev., (2013), 113:2244-2266.

[81] J. Yu, H. Ma, H. Yao, H. Cheng, R. Tong, Diastereoselective and regiodivergent oxa-[3 + 2] cycloaddition of Achmatowicz products and cyclic 1,3-dicarbonyl compounds, Org. Chem. Front., (2016), 3:714-719.
[82] M.D. Lewis, J.K. Cha, Y. Kishi, Highly Stereoselective Approaches to α- and β-C-Glycopyranosides, J. Am. Chem. Soc., (1982), 104:4976-4978.
[83] Honda T., Investigation of innovative synthesis of biologically active compounds on the basis of newly developed reactions, Chem. Pharm. Bull., (2012), 60:687-705.
[84] Honda T., N. Sano, Kanai K., Concise enantioselective synthesis of (+)-asperlin by application of the Sharpless kinetic resolution to 2-furylmethanol derivatives bearing alkenyl moiety on the side chain, Heterocycles, (1995), 41:425-429.
[85] B. Chen, X. Liu, Y.-J. Hu, D.-M. Zhang, L. Deng et al., Enantioselective total synthesis of (-)-colchicine, (+)-demecolcinone and metacolchicine: determination of the absolute configurations of the latter two alkaloids , Chem. Sci., (2017), 8:4961–4966.
[86] S.F. Martin, D.E. Guinn, Stereoselective synthesis of (+)-Prelog-Djerassi lactone from furanoid intermediates, J. Org. Chem., (1987), 52:5588-5593.
[87] S.F. Martin, D.E. Guinn, Prelog-Djerassi lactonic acid. A target for design and development of stereoselective synthetic methods, Synthesis, (1991), 1991:245-262.
[88] H. Guo, G.A. O'Doherty, De novo asymmetric synthesis of D- and L-swainsonine, Org. Lett., (2006), 8:1609-1612.
[89] M. Mondon, J.P. Gesson, Asymmetric synthesis of styryl-lactones, Curr. Org. Synth., (2006), 3:41-75.
[90] Z. Li, T.F. Leung, R. Tong, Total syntheses of (+/-) musellarins A-C, Chem Commun., (2014), 50:10990.
[91] Z. Li, F.C.F. Ip, N.Y. Ip, R. Tong, Highly trans-selective arylation of Achmatowicz rearrangement products by reductive γ-deoxygenation and Heck–Matsuda reaction: asymmetric total synthesis of (-)-Musellarins A–C and their analogues, Chem. Eur. J., (2015), 21:11152 – 11157.
[92] A.T. A.T. Herrmann, S.R. Martinez, A. Zakarian, A concise asymmetric total synthesis of (+)-brevisamide, Org. Lett., (2011), 13:3636-3639.
[93] K.C. Nicolau, Q. Kang, S.Y. Ng, D.Y.K. Chen, Total synthesis of engelrin A, J. Am. Chem. Soc., (2010), 132:8219-8222.
[94] R.H. Pouwer, J.-A. Richard, C.-C. Tseng, D.Y.-K. Chen, Chemical synthesis of the engelrins, Chem. Asian J., (2012), 7:22-35.
[95] R.A. Jones, M.J. Krische, Asymmetric total synthsesis of the iridoid β-glucoside (+)-geniposide via phosphine organocatalysis, Org Lett., (2009), 11:1849-1851.
[96] M.H. Haukaas, G.A. O'Doherty, Synthesis of D- and L-Deoxymannojirimycin via an asymmetric aminohydroxylation of vinylfuran, Org. Lett., (2001), 3:401-404.
[97] C.A. Leverett, M.P. Cassidy, A. Padwa, Application of the aza-Achmatowicz oxidative rearrangement for the stereoselective synthesis of the Cassia and Prosopis alkaloid family, J. Org. Chem., (2006), 71:8591-8601.
[98] W.-S. Zhou, Z.-H. Lu, Y.-M. Xu, L.-X. Liao, Z.-M. Wang, Synthesis of optically active α-furfuryl amine derivatives and application to the asymmetric syntheses. Tetrahedron (1999), 55 , 11959-11983.]
[99] B. Mucha, H. Martin, R. Hoffmann, Improved procedure for the synthesis of 6-alkoxy-2,3-dihydro-6H-pyran-3ones (2,3-dideoxy-DL-pent-2-enopyranos-4-uloses). Neat conversion into polyfunctionalized cyclopentenones, Tetrahedron Lett., (1989), 30:4489-4492.
[100] H.C. Kolb, H. Martin, R. Hoffmann, A total synthesis of racemic and optically active terrein (trans-4, 5-dihydroxy-3-[(E)-1-propenyl]-2-cyclopenten-1-one) , Tetrahedron: Asymmetry, (1990), 1:237-250.
[101] C. Jimenez, Marine natural products in medicinal chemistry, ACS Med. Chem. Lett., (2018), 9:959-961.
[102] F. Li, Y. Wang, D. Li, Y. Chen, Q.P. Dou, Are we seeing a resurgence in the use of natural products for new drug discovert?, Exp. Opin. Drug Discov., (2019), 14:417-420.
[103] K.C. Nicolaou, R.J. Aversa, Maitotoxin: an inspiration for synthesis. Isr. J. Chem., (2011), 51:359-377.
[104] K.C. Nicolaou, M.O. Frederick, R.J. Aversa, The continuing saga of the marine polyether biotoxins, Angew. Chem. Int. Ed., (2008), 47:7182-7225.
[105] K.C. Nicolaou, R.J. Aversa, J. Jin, F. Rivas, Synthesis of the ABCDEFG ring system of maitotoxin, J. Am. Chem. Soc., (2010), 132:6855-6861.
[106] A.S. Makarov, M.G. Uchuskin, I.V. Trushkov, Furan oxidation reactions in the total synthesis of natural products, Synthesis, (2018), 50:3059-3086.
[107] G. Zhao, R. Tong, A solvent-free catalytic protocol for the Achmatowicz rearrangement, Green Chem,. (2019), 21:64-68.
[108] G. Zhao, R. Tong, Silica gel enables Achmatowicz rearrangement with KBr/oxone under "anhydrous" condition for one-pot functionalization, Tetrahedron, (2019), 75:1669-1675.
[109] R.J. Ferrier, J.O. Hoberg, Synthesis and reactions of unsaturated sugars, Adv. Carbohydr. Chem. Biochem., (2003), 58:55-119.
[110] N.M. Xavier, A.P. Rauter, Sugars containing α,β-unsaturated carbonyl systems: synthesis and their usefulness as scaffolds in carbohydrate chemistry, Carbohydr. Res., (2008), 343:1523–1539.
[111] B. Fraser-Reid, J.C. Lopez, Unsaturated sugars: a rich platform for methodological and synthetic studies, Curr. Org. Chem., (2009), 13:532-553.
[112] S. Kusumi, K. Sasaki, S. Wang, T. Watanabe, D. Takahashi, K. Toshima, Effective and chemoselective glycosylations using 2,3-unsaturated sugars, Org. Biomolecul. Chem., (2010), 8:3164-3178.
[113] A.M. Gómez, F. Lobo, C. Uriel, J.C. López, Recent developments in the Ferrier rearrangement, Eur. J. Org. Chem. (2013), 2013:7221–7262.
[114] L.V.R. Reddy, V. Kumar, R. Sagar, A.K. Shaw, Glycal-derived δ-hydroxy α, β-unsaturated aldehydes (Perlin aldehydes): versatile building blocks in organic synthesis, Chem. Rev., (2013), 113:3605-3631.
[115] G. Grynkiewicz, W. Szeja, P. Krzeczyński, A. Rusin, Hexenoses in design of glycoconjugates – from chemistry to function, Chem. & Biol. Interface, (2014), 4:301-320.
[116] A.M. Gómez, F. Lobo, S. Miranda, J.C. López, A survey of recent synthetic applications of 2,3-dideoxy-hex-2-enopyranosides, Molecules, (2015), 20:8357-8394.
[117] X. Liu, P. Carr M.G. Gardiner, M.G. Banwell, A.H. Elbanna et al., Levoglucosenone and its pseudoenantiomer iso-levoglucosenone as scaffolds for drug discovery and development, ACS Omega, (2020), 5:13926-13939.
[118] H. Guo, G.A. O'Doherty, De novo asymmetric synthesis of the anthrax tetrasaccharide by a palladium-catalyzed glycosidation reaction, Angew. Chem. Int. Ed., (2007), 46:5206-5208.
[119] H.-Y. L. Wang, G.A. O'Doherty, Modulators of Na/K-ATPase: a patent review, Expert Opin. Ther. Patents, (2012), 22:587-605.
[120] C. Bonini, G. Righi, A critical outlook and comparison of enantioselective oxidation methodologies of olefins, Tetrahedron, (2002), 58:4981-5021.
[121] V. Bhat, E.R. Welin, X.L. Guo, B.M. Stoltz, Advances in stereoconvergent catalysis from 2005–2015: transition-metal-mediated stereoablative reactions, dynamic kinetic resolutions, and dynamic kinetic asymmetric transformations, Chem. Rev., (2017), 117:4528-4561.
[122] M.A. Ciufolini, C.Y. Wood, The aza-Achmatowicz rearrangement: a route to useful building blocks for N- containing structures, Tetrahedron Lett., (1986), 27:5085-5088.

Article reviewed
Received: 28.10.2020 r./Accepted: 09.11.2020 r.

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DOI: 10.15199/180.2020.4.3

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MODERN SOLUTIONS OF BARNS FOR DAIRY CATTLE ON THE BASIS OF WOLF SYSTEM SUGGESTIONS

ROZWIĄZANIA NOWOCZESNYCH OBÓR DLA KRÓW MLECZNYCH NA PRZYKŁADZIE PROPOZYCJI WOLF SYSTEM

Summary: *Modern livestock buildings should ensure the appropriate environmental conditions. The following factors, affecting the environmental conditions were discussed: functionality of the buildings, microclimate of the premises, management technology, housing system and livestock building. The solutions of Wolf System, and in particular, the suggestions of free-stall, boxed littered and non-littered cattle barns and littered barns with the self-flowing bed system were presented. In the buildings with the mentioned solutions, there is a correct microclimate owing to the manually or automatically operated ventilation systems.*

Keywords: *cattle barn, functionality, microclimate, ventilation, construction*

Streszczenie: *Nowoczesne budynki inwentarskie powinny zapewniać odpowiednie warunki środowiskowe. Omówiono czynniki kształtujące warunki środowiskowe do których zaliczono: funkcjonalność budynków, mikroklimat pomieszczeń, technologię chowu, system utrzymania, budynek inwentarski. Przedstawiono rozwiązania Wolf System, w szczególności propozycje obór wolnostanowiskowych boksowych ściółkowych, bezściółkowych oraz z podłożem samospławialnym. W budynkach z takimi rozwiązaniami panuje właściwy mikroklimat dzięki systemom wentylacyjnym sterowanym ręcznie lub automatycznie.*

Słowa kluczowe: *obora, funkcjonalność, mikroklimat, wentylacja, konstrukcja*

Introduction

Cattle husbandry is one of the most important branches of agricultural production in Poland. Dairying has been always considered as one of the strategic sectors of food economy. The participation of cattle management in global agricultural production constitutes 19%, including ca. 16% for milk production and 3.4 % for beef production. The participation in commercial agricultural production is equal to 24% in total, including 19% for milk and 5.0% for beef.

Our country is a leading milk producer in Europe; in respect of the production level, it occupies the 4th place from among the EU countries (after Germany, France and Great Britain). There are, however, certain differences in the production concentration and milk performance of the total cow population in Poland as compared to the remaining EU countries. As a result of the so-far effective work on genetic improvement of our cows in the country, their production performances are almost equal to the results, obtained from the cows in the countries of the former EU (25 countries). The mean milk yield in Poland in 2019 from the herds of active population (cows under milk recording system) was equal to 8 530 kg [PFHBiPM, 2019]. The barns covered with the milk recording tested by ITP (Institute of Technology and Life Sciences) have the mean annual milk performance at the level of 7350 kg. Therefore, when having the cows, valuable in respect of genetics in our country, we should take care of the improvement of their welfare *via* betterment of environmental conditions and, in particular, in respect of cattle management techniques.

Production effects obtained from the cattle are a result of the impact of genetic and environmental factors, from among of which the following ones should be distinguished: functionality of buildings and functional courses, microclimate of premises, management technology, housing system and livestock building.

One of the most important scientific tasks of the contemporary agricultural engineering in respect of cattle production includes development and improvement of technique, employed in dairy cattle management in modern agricultural family farms and farming enterprises.

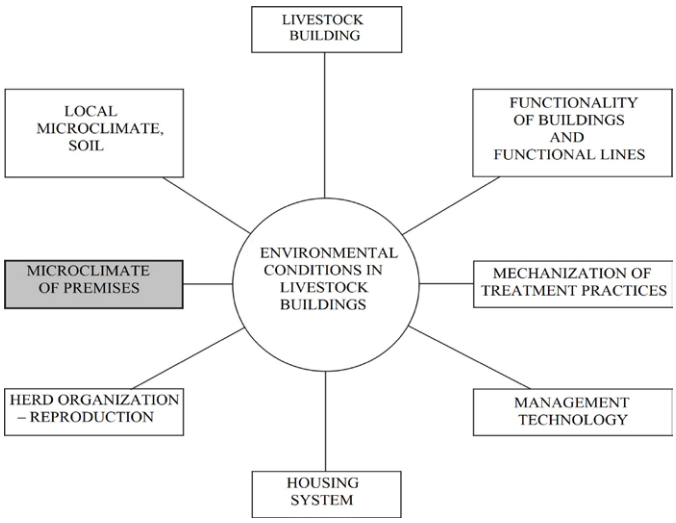
Apart from the important biological factors, the technique used in cattle management, including the activity in respect of building, mechanization and technology, determines effectiveness of milk production in a great degree. Functional livestock building such as cattle barn, should ensure the welfare to the animals, their high production performance

and good health state *via* the optimum environmental (mainly microclimate) conditions.

Under the differentiated climatic conditions of Poland, the cattle barn is an indispensable and, simultaneously, expensive object of the farm's infrastructure, which should ensure the mentioned above effectiveness owing to appropriate organization of the particular functional courses and technological lines: preparation of feeds and their supply, milking and cooling of milk and removal and storage of manure, and creation of optimum microclimatic environment in the zone of animals' staying.

Since 1999, the Institute of Building, Mechanization and Electrification of Agriculture (IBMER) and since 2010 (after reorganization), the Institute of Technology and Life Sciences has conducted a continuous field work on improvement of mechanization and technology and the environmental conditions in respect of cattle management which are mainly focused on free-stall cattle barns.

Fig. 1. Factors, shaping the environmental conditions in the livestock building for cattle [2]



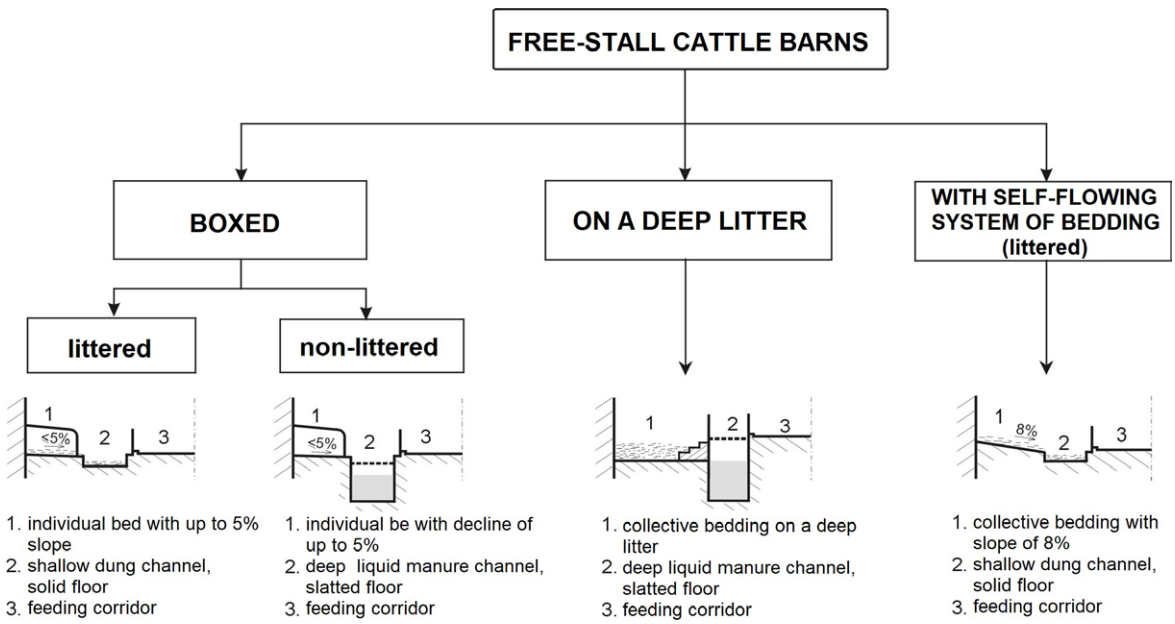
The most important factors, shaping the environmental conditions in the barns for the dairy cows are illustrated in Fig. 1.

Brief characteristics of the mentioned above factors:

1) Livestock building, in this case cattle barns: architecture, construction, roof, floor, walls, bedding, area and space (cubature) per one animal, auxiliary premises;
2) Functionality of the interior of the building and collision-free combination with mobile standing equipment, auxiliary rooms and functional courses of feeding and drinking supply, milking and milk cooling and receipt, straw spreading on beds, and removal and storage of manure, release of animals to the enclosures and cattle yards and in summertime – to the pastures;
3) Mechanization and automation of technological lines (including robotization): feeding and drinking supply, milking and milk cooling, removal and storage of manure;
4) Management technology connected with the production operations in technological lines;
5) Systems of cow housing: illustrated in Fig. 2.
6) Organization of herd: in a closed or open cycle, ensuring the parturition place for the cows and newborn calves;
7) Microclimate of the premises for the housed cows: requirements concerning temperature, relative humidity, admitted concentration of harmful animal gases (CO_2, NH_3, H_2S), value of air cooling down, velocity of air movement, contamination with the dust particles and microorganism, warm retention of baffles, lighting, heating in the auxiliary rooms and milking parlour, noise level, ventilation system and the appropriate air exchange;
8) Protection from negative effect of local climate, especially in autumn-winter season.

In view of the animal welfare and management effectiveness, the free-stall cattle barns have been recently preferred. Technological solutions of free-stall cattle barns in Poland are given in Fig. 2.

Fig. 2. Scheme of classification of free-stall cattle barns according to the housing systems. Source: own elaboration



Free-stall housing system, with the regulated access to the outside run, consists in keeping the cows without ties, mainly in boxes. Box housing consists in separation of the rest function for the cows from the function of their feeding. In the free-stall system, littered or non-littered boxes are employed. Boxes are covered with cut straw, sawdust, peat, river sand and separated solid fraction of liquid manure (slurry). The non-littered boxes have a soft rubber covering, called mattress.

Nowadays, the following free-stall littered barns with the grouped housing in the collective pens, with individual beds, are introduced:

- Individual boxes with littered beds or rubber mattresses in the littered and non-littered system;
- On a deep litter in the rest course;
- On a deep litter with the separated feeding-dung channel on a slatted floor;
- Littered beds with self-flowing (self-cleaning) system and dung-walking corridor on a solid floor;
- According to the WOLF SYSTEM projects, in deep free-stall boxes, covered with the separated solid fraction of liquid manure. Natural manure is removed from walking runs, using mechanical scrapers to a special channel, situated transversally in relation to the barns. Near the transverse channel, a closed construction separator separates a solid fraction up to min. 35% dry matter content of the slurry. Such fraction serves for a direct covering of the boxes twice a week.

In the free-stall housing system, the cows are always milked in the milking parlour by milking machine or by milking robots; the cows are directed to the milking parlour by the specially fenced off corridors.

The most important advantages of free-stall barns include:

- The higher number of cows, served by one operator;
- Easier human labour, especially in the case of milking (when milking is carried out by robot, the operators have only to supervise the robot who performs the whole work automatically);
- Better hygiene of milking;
- Conditions of cow housing correspond to their natural needs and welfare;
- Better possibilities of production mechanization and automation;
- The possibility of greater concentration of herds in the barn and introducing the computer-based management system in respect of herd organization, breeding selection, reproduction regulation, reasonable feeding with multi-componential feeds, milking hygiene and health state (udders and reproduction organs).

In the free-stall system of cattle housing, the highest level of mechanization and automation of production process may be obtained via introduction of the mentioned above computerized system of herd management which has been already introduced in a part of the barns, tested by Institute of Life Sciences and Technology (ITP).

In cattle management, we may observe a progress in effectiveness, especially in the newly constructed objects and in the old modernized ones, in farms with a higher area, having more than 50 ha. The constructed new objects in greater farms are usually free-stall barns. The older objects, as being erected in the 70ties and the 80ties are actually modernized, developed and adapted also to the free-stall cow housing system.

The mentioned above activities are accompanied by the increase in the concentration of herd, specialization of production, complex mechanization of particular production operations, rationalization of feeding with the concentrates via new preservation technologies and automatic feed mixing. The modern milking system in the milking parlours and cooling down of milk in a closed system improves perfectly the hygiene of milking and the quality of raw milk.

The aim of the paper

The aim of the work was to analyze and evaluate the existing solutions of the objects in cattle management and, in particular, functionality of barns, housing systems, milking and milk cooling procedures, preparation of feeds, feeding and drinking of animals, removal and storage of faeces as well as microclimate in the premises for animals and in the milking parlour, including the suggestion of modern solutions, on the example of barns, constructed in WOLF system.

The suggested solutions of WOLF SYSTEM (Fig.3 – 10)

The submitted solutions are modern and effective, ensuring the welfare and appropriate climate for the animals, safe and hygienic condition of the service work and a high level of mechanization in milk production.

Fig. 3. Cross-section of free-stall cow barn with steel-steel construction with intermediate pillars. Source: Wolf System

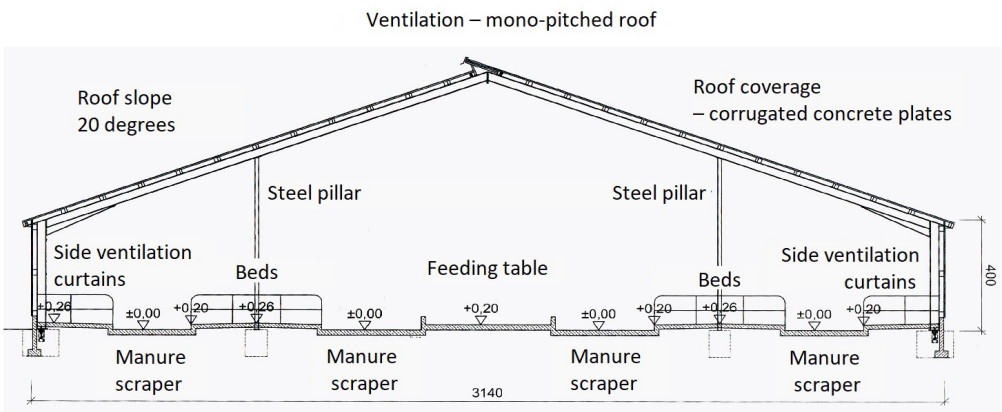


Fig. 4. Free-stall boxed barn with a slatted floor and channels for manure, side and roof ventilation with additional light. Source: Wolf System

Fig. 5. Side view of the barn with mechanically operated ventilation curtains. Source: Wolf System

Fig. 6. System of roll-up curtains, opened from the top, with electric or manual drive

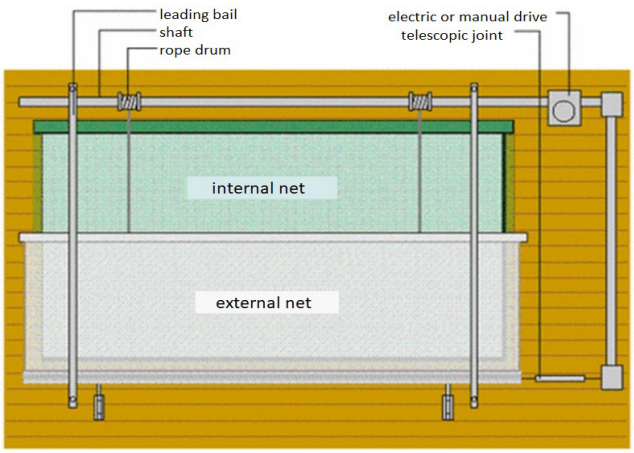
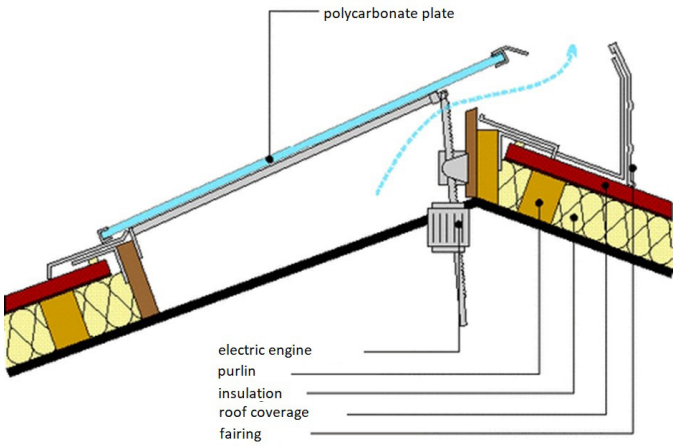


Fig. 7. Automatic control of exhaust channel of roof, using weather sensors a) with the thermal insulation of the roof, b) without insulation, without weather control device Source: Wolf System



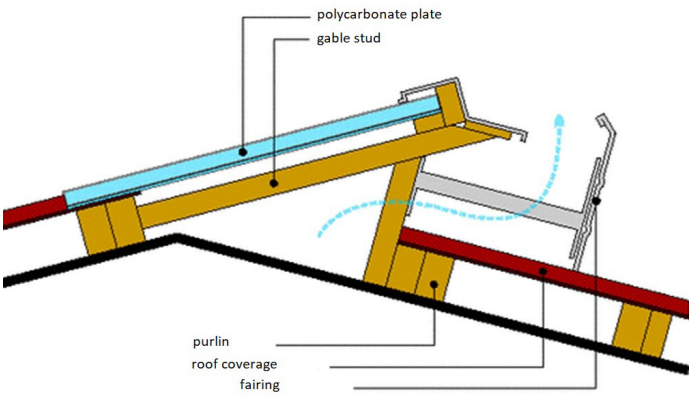


Fig. 8. View of boxed cattle barn, with polycarbonate skylights, with manure scrapers, roof ridge ventilation; side walls made in a form of net curtains, with a full PCV membrane. Source: Wolf System

Fig. 9. Littered barn with self-flowing system and mechanical manure scraper and ridge ventilation and polycarbonate curtains; construction of the barn – steel-steel with intermediate pillars. Source: Wolf System

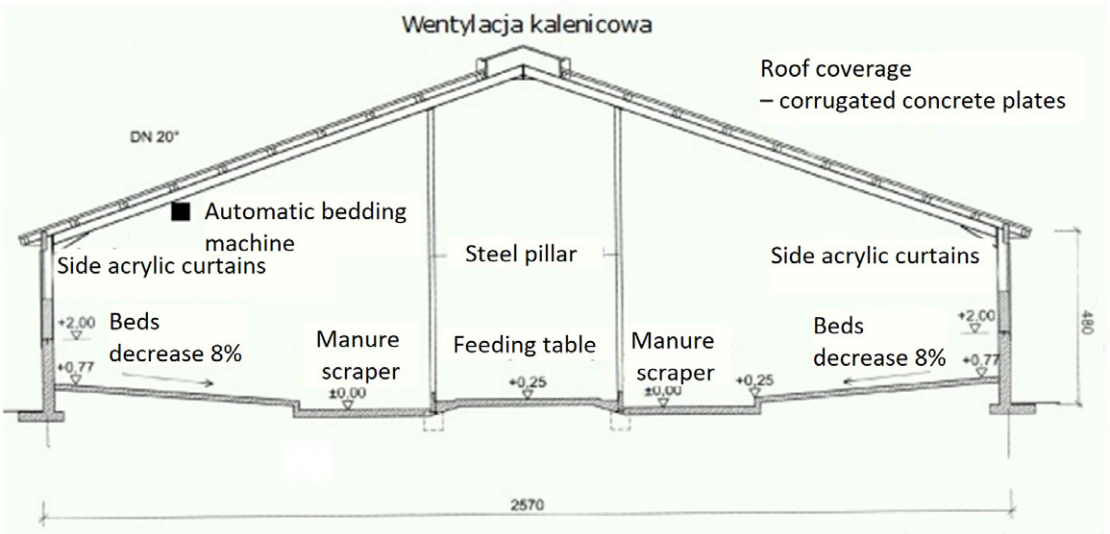


Fig. 10. View of free-stall boxed non-littered barn by Wolf System. Source: Wolf System

Field tests of the microclimate conditions

The methodology of testing the parameters of microclimate was based upon branch standard BN-86/880-03 (Industrial Standard 1986).

The following equipment was employed:

- Thermal hygrometers (cable sensors) for measurement of air temperature and humidity; with concentrator, equipped with memory for data collection having a volume of 3600 records;
- T
- Mobile thermal hygro-barometers with internal memory for constant testing of temperature, relative humidity and atmospheric pressure;
- Double-gas measuring devices of recorders for determination of CO_2 and NH_3 concentration;
- Multi-gas measuring device iTX, measuring the concentration of harmful gases: methane (CH_4), ammonia (NH3), hydrogen sulphide (H_2S) and nitrogen oxide (NO).

The results of the tests of the barns for the dairy cows in respect of environmental conditions, including microclimate, as referred to in the solutions, given in Fig. 3, 4 and 9, are presented in Tab. 1.

Tab. 1. Parameters of microclimate in the tested barns

Type of barn /housing system	Tz Mean min. - max	Tw Mean min. - max	Wz Mean min. - max	Ww Mean min. - max	CO_2 Mean min. - max	NH_3 Mean min. - max
Boxed littered	5.1 1.7 -10.8	11.5 7.6-15.8	72 41-90.3	60.3 36-73.5	932.6 500 -1900	4.5 1-9
Boxed non-littered	18.32 12 -32	17.60 13-21.03	59.25 38.10-91	66.47 46.97-80.0	665.51 300-1500	6.1 2.3-13.6
Littered with self-flowing (cleaning) system	23.1 15.3 -30.5	24.5 17.7-29.0	60.5 30.5-90.7	65.96 41.1-79.9	818 400-1600	4.23 1-9

Source: Own elaboration based upon: Mazur 2012, Romaniuk et al., 2012 [7]

Tz – air temperature outside the building [°C];
Tw – temperature inside the building [°C];
Wz – relative air humidity outside the building [%];
Ww – relative air humidity inside the building [%];
CO_2 – concentration of carbon dioxide CO_2 [ppm];
NH_3 – concentration of ammonia NH3 [ppm]

Summing up and conclusions

1. The suggested solutions meet the requirements for modern livestock barns for the cattle, i.e. ensuring as follows:
   - A sufficient space for the animals and equipment for mechanization and automation of production operations;
   - Functionality i.e. appropriate mutual situation of technological elements;
   - Efficient ventilation of barns with additional light in the roof ridge.
2. Such solutions ensure the following microclimatic conditions:
   - Mean carbon dioxide concentration, not exceeding 100 ppm, in relation to the limit, recommended value of 3000 ppm,
   - Mean ammonia concentration, not exceeding 10 ppm,
   - Mean air temperature during the period of summer heat, not higher than 25°C at relative air humidity not higher than 80%.
3. When choosing the most advantageous solution by the investor, e.g. of the dairy barn, we should be directed by the minimization of the operating costs for obtaining 1 litre of milk of the appropriate quality, with the consideration of the following limitations:
   - In respect of microclimate: concentration of $CO_2 \leq 3000$ ppm, concentration of $NH_3 \leq 20$ ppm, temperature not higher than 25°C and not lower than -4°C.
   - Level of mechanization V, characterized by labour outlays ≤ 5 working minutes $\cdot$ $DJP^{-1} \cdot 24h^{-1}$.

References

[1] Norma Branżowa BN-86/880-03 Mikroklimat w budynkach inwentarskich, BN-86/880-03, Wydawnictwa Normalizacyjne „Alfa", s. 287–290.
[2] Romaniuk W. Fiedrowicz G., Biskupska K. 2011, Analiza standardów technologicznych obór dla krów mlecznych w gospodarstwach rodzinnych i farmerskich, Monografia, ITP Falenty, ss.66.
[3] Polska Federacja Hodowców i Producentów Mleka 2019, Ocena i hodowla bydła mlecznego. Dane za rok 2019, ss.193, https://pfhb.pl/fileadmin/user_upload/OCENA/publikacje/publikacje_2020/PFHBiPM_Wyniki_poglad_2020_WEB.pdf
[4] Romaniuk W. Mazur K. Domasiewicz T. Wardal W.J., Biskupska K. 2012, Kształtowanie warunków środowiskowych w chowie bydła mlecznego – stan istniejący i propozycje przebudowy, ss. Monografia, Inżynieria w Rolnictwie nr 4, ITP Falenty, ISBN: 978-83-62416-36-3, ISSN 2083-9545, ss.92.
[5] W. Romaniuk, W. Mazur K., Reichel R. 2015, Suzdal.
[6] W. Romaniuk, W. Mazur K., Reichel R. 2015. Проектирование решений вентиляции в современных коровниках для дойных коров, p. 454-465, chapter in monograph: Инновационные Технологии В Адаптивно-Ландшафтном Земледелии, ФГБНУ Владимирский НИИСХ, Suzdal, Russia ISBN 978-5-9906871-3-4.
[7] Mazur K., Romaniuk W. 2015. Book of Full Papers of International Scientific XXXVI CIOSTA & CIGR Section V Conference, Saint Petersburg – PUSHKIN, 25-28.05.2015, Environmentally Friendly Agriculture And Forestry For Future Generations, p.539-571

Article reviewed
Received: 14.10.2020 r./Accepted: 17.11.2020 r.

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THE POLE WHO INVENTED A NEW METHOD OF WEAVING, BULLET-RESISTANT VEST AND....TV

POLAK, KTÓRY WYNALAZŁ NOWY SPOSÓB TKANIA, KAMIZELKĘ KULOODPORNĄ I... TELEWIZOR

Summary: *Jan Szczepanik, Polish inventor was called, inter alia, "Polish Edison", and "Austrian Edison". At the breakdown of the 19th century, Mark Twain described his activity in two papers. Jan Szczepanik was the author of at least 50 inventions and several hundred technical patents in the field of coloured photography, weaving or television.*

Keywords: *Jan Szczepanik, coloured photography, weaving, television, photometer, colorimeter*

Streszczenie: *Jan Szczepanik – polski wynalazca, nazywany m. in. „polskim Edisonem", „austriackim Edisonem". Na przełomie XIX i XX w. Mark Twain opisał jego działalność w dwóch artykułach. Jan Szczepanik był autorem co najmniej 50 wynalazków i kilkuset opatentowanych pomysłów technicznych z dziedziny fotografii barwnej, tkactwa czy telewizji.*

Słowa kluczowe: *Jan Szczepanik, fotografia barwna, tkactwo, telewizja, fotometr, kolorymetr*

The beginning of the era of inventions – without the Poles. Luckily, not for long

At the middle of the 19th century, when the fundamental discoveries and inventories, determining the shape of the today civilization were generated, the young and clever Poles had the only one aim: independence of the Fatherland. Therefore, the names of the young Americans, Englishmen, Germans or French people were memorized in outstanding scientific publications or in the patent offices where the names of their Polish contemporaries could be found on the plates, marking the insurrectionary graves.

Fortunately, the mentioned striving at giving the life for the struggle for independence was somewhat decreased at the breakdown of the 19th century; the other aim appeared, including also striving at betterment of scientific and technical creativeness. It was followed by quick successes. In **1883**, Karol Olszewski and Zygmunt Wróblewski as the first in the world liquefied oxygen and nitrogen; Albert Einstein utilized the achievements of Marian Smoluchowski as the basis of his work; the inventory of Julian Ochorowicz saved Eiffel Tower.... the examples may be multiplied. However, **Jan Szczepanik** was undoubtedly the most fertile **inventor** of the discussed period.

Fig. 1. Jan Szczepanik [6]

Polish Edison

His contemporaries were so much enchanted in his innovative technical solutions that American journalist (and writer) Mark Twain called him Edison. It was the highest compliment as this

Fig. 1. Excerpt from the article "The Austrian Edison Keepeing School Again" Mark Twain's article about Jan Szczepanik [6]

THE AUSTRIAN EDISON KEEPING SCHOOL AGAIN.

BY MARK TWAIN.

BY a paragraph in the "Freie Presse" it appears that Jan Szczepanik, the youthful inventor of the "telelectroscope" [for seeing at great distances] and some other scientific marvels, has been having an odd adventure, by help of the state.

Vienna is hospitably ready to smile whenever there is an opportunity, and this seems to be a fair one. Three or four years ago, when Szczepanik was nineteen or twenty years old, he was a schoolmaster in a Moravian village, on a salary of—I forget the amount, but no matter; there was not enough of it to remember. His head was full of inventions, and in his odd hours he began to plan them out. He soon perfected an ingenious invention for applying photography to pattern-designing as used in the textile industries, whereby he proposed to reduce the customary outlay cf time, labor, and money expended on that department of loom-work to next to nothing. He wanted to carry his project to Vienna and market it, and as he could not get leave of absence, he made his trip without leave. This lost him his place, but did not gain him his market. When his money ran out he went back home, and was presently reinstated. By and by he deserted once more, and went to Vienna, and this time he made some friends who assisted him, and his invention was sold to England and Germany for a great sum. During the past three years he has been experimenting and investigating in velvety comfort. His most picturesque achievement is his telelectroscope, a device which a number of able men—including Mr. Edison, I think—had already tried their hands at, with prospects of eventual success. A Frenchman came near to solving the difficult and intricate problem

genial American inventor has more than one thousand patents on his account, so he enjoyed a merited fame. In truth, when writing about Jan Szczepanik, Mark Twain called him **Austrian** Edison because he met him in Vienna and the subtleties concerning Austria and Poland (under partition) were not understandable for the American mind. Therefore, the paper written by Twain and published in the monthly „*The Century Illustrated Magazine*" (August 1898, New York) had the title „*The Austrian Edison Keeping School Again*". Later on, Mark Twain wrote once again (in superlatives!) about the method of a distance transmitting of images, that is, precursor of television, invented by Szczepanik; it was found in the futuristic story „*From London to Times 1904*", published in November 1898. Let's pay attention to the fact that M. Twain tried to anticipate how the world would look like after passing the border of the 19th century. And the inventions of Szczepanik played quite significant role in his vision.

From rural school to the elite of the inventors

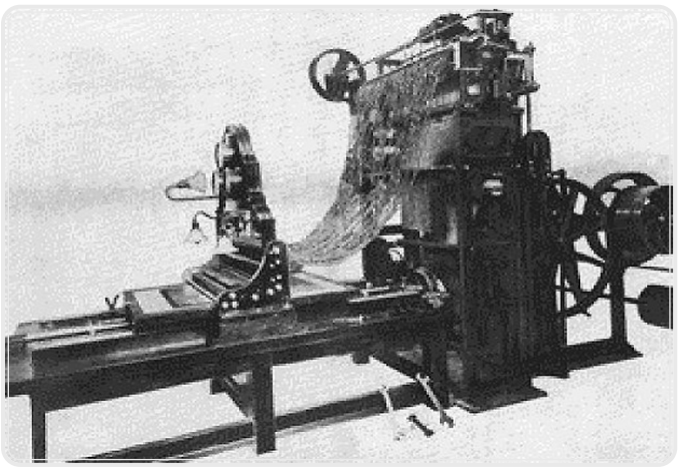
Szczepanik was, of course, a native Pole. He was born in Rudniki (Mościska poviat), he grew up in Krosno, he commenced gymnasium in Jasło and finished in Cracow; he studied in "Teacher Seminar", also in Cracow. Later on, he was a teacher in schools of the Krosno province and he could live there until the end of his life as a rural teacher.

However, when having a talent and temperament of inventor, Szczepanik interrupted his career as a rural teacher and came back (in **1896**) to Cracow. He was interested in combination of photography (which was taking then the first steps) and coloured weaving, so he worked simultaneously at the shop of the Weavers' Association and in a photographic shop of Ludwik Kleinberg. The mentioned two ideas were developing in parallel in the mind of Szczepanik although they were mutually strengthening and supplementing.

Photography and weaving

When working at Kleinberg shop, Szczepanik improved the existing pioneer methods of coloured photography. The success came later. He performed the photos on black-white film (as only such existed at that time) but he employed coloured filters (red, green and blue). The discussed achievement brought the results later and they were real, meaningful successes. In **1899**, he developed a system of miniature coloured film on which he obtained British patent in **1900**. He invented also a technique of obtaining a coloured photographic paper; he produced it and sold under his own name.

Fig. 3. The world's first automatic weaving machine - the invention of Jan Szczepanik [7]



On the other hand, the success connected with weaving came earlier. As early as in **1896** (the year of arriving to Cracow), Szczepanik created a prototype of weaving machine, producing patterned wall-hanging carpets on the basis of photography. It is worthy to remind that the coloured patterned fabrics were already mechanically produced (earlier, it was a manual work of weaver) using the so-called Jacquard looms (weaving machine), invented by Joseph Maria Jacquard. In the mentioned machines, the process of weaving was mechanically controlled by a program in a form of perforated cards. The cards had to be produced manually by the workers and often the mistakes had place. Szczepanik developed the method for automatic punching the cards on the grounds of photography of the designed pattern of fabric; he constructed also the electric system for reading of the mentioned cards and controlling the work of the weaving machine. The inventory was enthusiastically approved and as early as in 1896, Szczepanik obtained the Austrian, German and English patent and later on, the American patent for his inventory.

Vienna career

His employer Kleinberg appreciated highly talents of Szczepanik and enabled him visit to Vienna in 1898. It was a very good decision. Cracow was a provincial city of Austrian-Hungarian monarchy whereas in the capital city, it was possible to arrange advantageous contacts and develop the innovative ideas. Kleinberg established a special Society in Vienna, with the name „*Societe des Inventions Jan Szczepanik et Compagnie*" which took case of propagation and promotion of the inventories of Szczepanik. As a result of such activities of the mentioned Society and the support of business, there were established the factories of wall-hanging carpets, situated in Brussels, Roubaix and in Wuppertal and employing the weaving machines, invented by Szczepanik. Finally they were also erected in Cracow. It happened that the inventory of Jan Szczepanik found the way to its "birth" place, although by the roundabout way!

Fig. 4. Jan Szczepanik at the factory in Barmen [10]

Szczepanik knew how to care of his business. In 1898, there was a jubilee of the 50th anniversary of reigning by Emperor Franz Joseph, so Szczepanik designed and performed (in 4 copies) a wall carpet, representing the Ruler. He entitled it "Apotheosis" and offered to the Emperor. In effect, his wall carpets began to be fashionable among the Vienna aristocracy and Szczepanik became famous and rich. Mark Twain – who met the inventor in Vienna in 1898 and wrote the mentioned above publications about Szczepanik – received also a gift from the artist in a form of the writer's woven portrait.

Underestimated idea of television

When he had learned the transmission of the image between the photography and weaving machine, Szczepanik got an idea to transmit the images at a distance for the people, i.e. he discovered the principle of television.

As early as in **1897**, he obtained the British patent (no 5031) for "telectroscope, that is, a device for reproduction of images at a distance, using electricity". The first public transmission of the image at the distance occurred in Vienna in 1896 and the object, the image of which was to be transmitted, was the Saint Charles Borromeo Vienna Church. The journalists who observed the transmission few streets away, were impressed by the discussed event although many people had doubts whether it was a real image transmitted at the distance. In effect, the show of telectroscope didn't cause such impression in Vienna as it should do.

Fig. 5. Excerpt from the article Dr. Johannes Horowitz about Jan Szczepanik , "That New Telectroscope", The New York Times, 3 April 1898 [8]

NEW YORK TIMES, S

THAT NEW TELECTROSCOPE

Details of the Instrument That Is to Transmit Pictures Over a Telegraph Wire.

SZCZEPANIK'S WEIRD MACHINE

Claims of the Polish Schoolmaster as to What His Telectroscope Will Do and How It Does It—A Scheme for the Transmission of Colored Rays.

VIENNA, March 21.—The invention of the telectroscope, or "far-seer," is causing a very considerable sensation in the scientific world. Jan Szczepanik, the young inventor, is now here. From an interview had with him it appears that the telectroscope is, if practicable, as it is claimed to be, something besides a mere toy, an instrument of practical importance, and its efficiency seems to be more considerable than could be judged from particulars hitherto published.

Szczepanik declares that the telectroscope will not only transmit pictures to a great distance, and reproduce them there, but also that it is possible that it will make the present telegraph instruments superfluous over short distances. The inventor claims that his instrument will not only transmit pictures of actual scenes, but will also almost instantaneously transmit reproductions of manuscripts or printed matter to a great distance and in a moment fix the image on a sensitive plate of paper at the receiving point. This transmission can take place, he asserts, to the same distances that the telephone will work.

Szczepanik claims that the telectroscope is already complete in every particular and ready for work. If some morning the first copy of a big Vienna daily newspaper were put into the apparatus, in a few seconds,

Nevertheless, the mentioned inventory was widely (and positively!) commented abroad, *inter alia*, in the USA, in the articles of the mentioned above Mark Twain. On April, 3, 1898, it was also found on a title page of "New York Times" journal. In 1900, Szczepanik submitted his inventory (in the improved version, called "telephoto') at the World Expo in Paris and he gained a quite great recognition. As a result, he was very near to obtaining a historic fame as inventor of television but his restless spirit directed him into completely different field.

Bullet-proof butler and Spanish nobility

The inventory of bullet-proof vest brought the international fame to Szczepanik. As we kwon – he was an expert in weaving – so in **1901**, he developed such structure made from multi-layer fabric which was able to take over the energy of the bullet and protected completely human body , hidden under the mentioned material. The first tests of the vest were carried out in 1901, at the yard of the Szczepanik study, situated at the Pragerstarsse in Vienna. The available photography on the Internet page shows the moment when the testing expert (Director Borzykowskl) shot – from the distance of 3 steps – from the 7 mm-calibre revolver, to a servant of Szczepanik, dressed in the described vest. Of course, the servant came out unharmed. The journalists wrote at length about "bullet-resistant" butler with admiration.

As early as one year after introducing the Szczepanik's fabric to the market, in 1902, it became so famous after the event of saving the life of Spanish King Alfonso XIII. Szczepanik became awarded with the Order of Catholic Isabel and Spanish nobleman dignity.

Fig. 6. The world's first bulletproof vest during tests (1901) - director of the Viennese workshop of J. Szczepanik - Mr. Borzykowski shoots the servant Jan (7 mm revolver, distance 3 steps) [9]

Fig. 7. A demonstration of the properties of the bulletproof vest during the First Polish Photographic Exhibition in Krakow in 1902. Eng. L. Sippel, captain Urbanski shoots. Photo from the magazine: "Ilustracya Polska" [10]

Due to the same reason, the tsar Nicolas II of Russia wanted to distinguish him with the Saint Anna Order but Szczepanik refused to receive the distinction from the aggressor, so the tsar gave him only a golden watch with diamonds and added also the broche with four diamonds and two sapphires for the fiancé of the inventor (he was only 30 years old at that time).

Coloured photography, coloured sound film and a lot of other patents

Szczepanik was the owner of ca. 100 patents in total. As it was mentioned above, he invented, inter alia, the methods of coloured photography (**1899**) and light-sensitive coloured paper which was produced by Swiss company J.K. Smith (since **1905**) but was also sold by Szczepanik i.e. by the company, containing his name in the name of the firm. He constructed the first camera

Fig. 8. Jan Szczepanik and his negative camera [7]

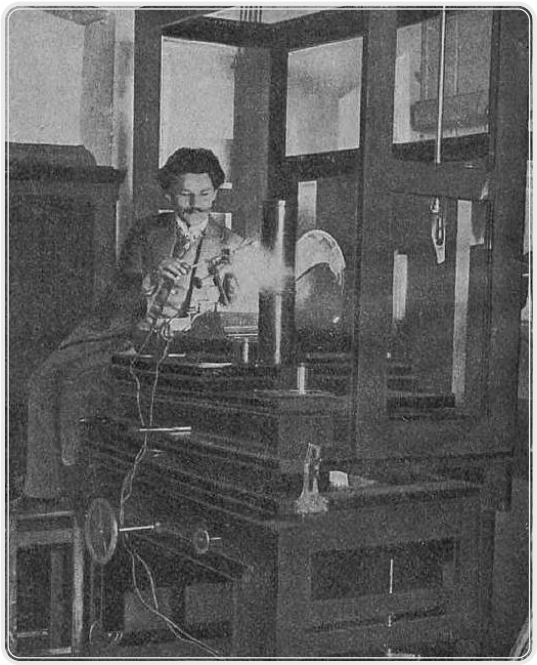


Fig. 9. The first model of Szczepanik's camera [13]

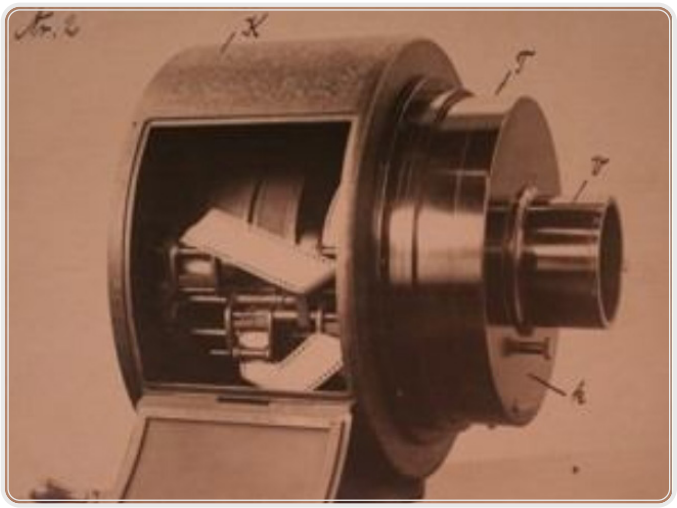
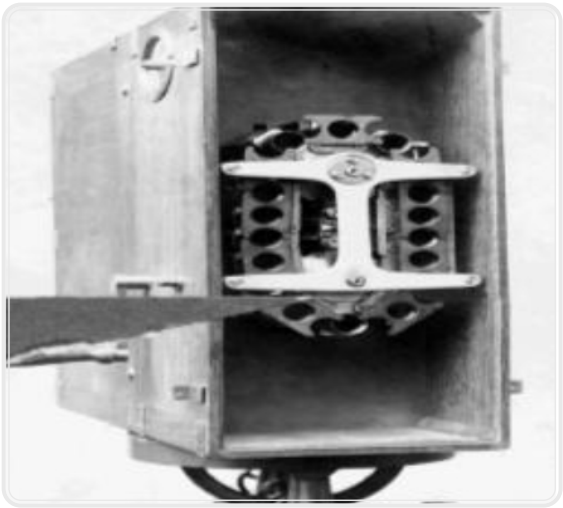


Fig. 10. The second model of Szczepanik's camera [7]



for producing the coloured films (**1915**) and projector adapted to displaying of such films. He alone produced also few coloured films; he should mention here "A Mountain Pass" (**1921**), made in the Alps; it was very highly appreciated. He produced also a scientific film, recording the course of surgical operation in the hospital Lagnebeck-Virchow in **1925**. Szczepanik was also the owner of the inventory connected with recording of sound on a film tape, using cathode rays and its reproduction with the use of photocell. His patent application was submitted on 25.02.1914 but the First World War was commenced and the patent was granted as late as in June, 15, 1920. Nevertheless, the system by Szczepanik has significantly contributed to creation and development of sound film.

He developed the appropriate equipment for the photography and film making purposes; it included *inter alia*, a **photometer** for measurement of light intensity and a **colorimeter** for measurement of intensity of the particular colours.

It was not all. In **1902**, Szczepanik constructed electric automatic gun, and in **1903** he introduced some improvement to the first radio equipment ("telegraph without wire"). The inventor worked also on the electronic devices for strengthening of sounds and the equipment which was called by him "photo sculptor" – it was used for photographic recording of three-dimensional objects, that is, it played then such role as to-day 3D scanners.

It is worthy, therefore, remembering "Polish Edison".

Bibliography

[1] Jan Szczepanik. Wikipedia. https://pl.wikipedia.org/wiki/Jan_Szczepanik dostęp 19.10.2020.
[2] Smoleńska L., Sroka M.: Wielcy znani i nieznani, Polski Edison – Jan Szczepanik (1872–1926), Wydawnictwo radia i telewizji, Warszawa 1988, str. 222–242.
[3] Włodek R.: Szczepanik Jan, Polski Słownik Biograficzny, zeszyt 193, Warszawa-Kraków 2010.
[4] Pragłowska A.: Obrazy i barwy. O wynalazkach i życiu Jana Szczepanika, Tarnów: S-CAN, 2012.
[5] Tadeusiewicz R.: Jan Szczepanik: polski Edison. Rzecz o Historii, Rzeczpospolita, 02.10.2020.
[6] https://bialczynski.pl/wielcy-polacy/jan-szczepanik-1872-1926-wynalazca-telewizji-filmu-barwnego-fotografii-barwnej-i-paru-innych-rzeczy/
[7] http://www.strony.toya.net.pl/~zse/patron/patwyn.html
[8] https://www.histv.net/szczepanik-new-york-times-1898
[9] https://www.wikiwand.com/pl/Kamizelka_kuloodporna
[10] https://krosno24.pl/informacje/galicyjski-geniusz-ktory-swoja-mlodosc-spedzil-w-krosnie-i2107
[11] https://www.forbes.pl/przywodztwo/jan-szczepanik-przedsiebiorca/r25qvxb
[12] https://www.podkarpackahistoria.pl/wiadomosci/662,jan-szczepanik-polski-edison-zwiazany-z-podkarpaciem
[12] https://www.wikiwand.com/pl/Jan_Szczepanik
[13] https://naszemiasto.pl/wielcy-tarnowianie-jan-szczepanik-genialny-wynalazca-z/ar/c13-4460210

Article reviewed
Received: 19.10.2020 r./Accepted: 12.11.2020 r.

THE POLISH ACADEMY OF SCIENCES
URGENT APPEAL ON THE ONGOING COVID-19 CRISIS

Source: https://institution.pan.pl/index.php/603-urgent-appeal-on-the-ongoing-covid-19-crisis
on 12 October 2020

The Interdisciplinary COVID-19 Advisory Team to the President of the Polish Academy of Sciences has just released a series of recommendations that should help prevent the further spread of the pandemic. The team appeals to employers, healthcare professionals, and all individuals to alter our attitudes and behavior to protect the most vulnerable members of society.

The first wave of COVID-19 affected Poland somewhat less severely than other countries due to the extensive, promptly implemented restrictions. However, as autumn progresses, we are seeing a rapid increase in SARS-CoV-2 infections, and, sadly, in deaths of patients suffering from COVID-19 caused by the virus. Many undiagnosed or asymptomatic people are infecting others, and the situation is starting to spiral out of control. We must realize that unless we all alter our dismissive attitudes and behaviors, on individual and collective levels, Poland's healthcare system will become completely overwhelmed within a month. We are already seeing shortages in hospital vacancies.

The danger this entails is that in the near future, people unable to access help and support may die at home or even on the streets. Forecasts indicate that the situation will worsen in the coming days. Even a complete lockdown would only start showing results in around two weeks' time. However, medicine and the economy are deeply intertwined; the costs of another lockdown would be enormous, and we should avoid this as much as possible. Government decrees or even declaring a state of emergency will not be sufficient to prevent the worst; it is up to us citizens to take action, to change our behavior to protect the most vulnerable members of society. You and I can take steps right now to protect ourselves and our families and friends, by adhering to the following recommendations.

Recommendations for all individuals:

1. Do not spit on or sneeze at the fate of your family, friends, acquaintances and strangers. Every breath exhaled through the nose and mouth releases tiny droplets of saliva and nasal secretions. They usually fall to the ground within about 1.5 meters of the individual. When someone speaks in a normal tone, the number of aerosol droplets and their range increase slightly. When they raise their voice, the range increases again, and when they are shouting or singing loudly, the

ABOUT THE TEAM

The Interdisciplinary COVID-19 Advisory Team to the President of the Polish Academy of Sciences was set up on 30 June 2020. The team is led by **Prof. Jerzy Duszyński**, President of PAS, with **Prof. Krzysztof Pyrć** (Jagiellonian University) acting as deputy. **Dr. Aneta Afelt** (University of Warsaw) is the secretary of the board. Other members are **Prof. Radosław Owczuk** (Medical University of Gdańsk), **Dr. Anna Ochab-Marcinek** (PAS Institute of Physical Chemistry), **Dr. Magdalena Rosińska** (National Institute of Public Health – National Institute of Hygiene), **Prof. Andrzej Rychard** (PAS Institute of Philosophy and Sociology) and **Dr. Tomasz Smiatacz** (Medical University of Gdańsk).

volume of droplets and their range are significantly greater. Aerosol droplets emitted by an infected person contain the SARS-CoV-2 virus, and they are the main route of infection. This is why perhaps the most important recommendation is to maintain a distance of at least 1.5 meters from other people and to wear a mask covering the nose and the mouth. If possible, any meetings in person should be held out in the open air, and travel should be avoided unless strictly necessary.

2. Make sure you wash your hands frequently, and use disinfectant when this is impossible.
3. If you feel unwell and think you may have a cold or flu, stay at home and do not meet others. Wait until all symptoms have passed, and ideally leave it a day or two longer. Contact your GP to check whether you should have a COVID-19 test.
4. If you have tested positive for COVID-19 or you have lost your sense of smell and/or taste, inform everyone you have had contact with between now and two days before the onset of symptoms. Although this is the duty of the public health & safety inspectorate, its highly overworked and exhausted staff may not be able to respond sufficiently fast.
5. If any of your child's schoolfriends or their parents have tested positive for COVID-19 (for example, if you have been so informed by their school or kindergarten), stay at home unless absolutely necessary, maintain strict social distancing at work, wear a mask, and wash and disinfect your hands frequently. If you or your child start experiencing even the mildest symptoms, contact your GP immediately. Avoid contact with vulnerable people.
6. If any of your friends or colleagues test positive for COVID-19, follow the advice given above.
7. Make an effort to help and support your friends and neighbors, especially those in difficult circumstances, while maintaining safety precautions. Act with a sense of solidarity!

Recommendations for employers or people responsible for others:

8. If any of your employees has a cold or has been in contact with a person infected with SARS-CoV-2, take the initiative to allow them to work remotely. This may help delay official quarantine measures.
9. Start introducing remote working as soon as possible. Don't forget that commuting to and from work on crowded public transport puts your employees at high risk of contracting SARS-CoV-2 or flu. Remote working will help reduce overcrowding on public transport, especially at peak times.
10. At the same time, remember only to follow restrictions and rules which are grounded in the latest scientific information, rather than in your own personal beliefs or emotions.
11. Make sure any restrictions are communicated clearly and are simple to follow.
12. Excessive or incomprehensible restrictions are generally ignored, and may have the opposite effect to that intended.
13. It is key that you set a good example to your employees. If you fail to follow health & safety precautions or quarantine rules, your staff will follow your lead.

Recommendations for senior citizens and vulnerable individuals:

14. Avoid crowded places and try to keep contact with others to minimum, even your children and grandchildren.
15. Limit your social interactions.

Recommendations for all healthcare professionals:

16. Always remember that your job as a doctor, nurse, or other healthcare professional carries a certain responsibility. Never assume that the fight against COVID-19 does not concern you. By using personal protective equipment, you can continue caring for your patients. Whenever possible, promptly attend to any patients seeking care.

Remember: by following these recommendations, you are protecting yourself, your family and friends. If we all strictly adhere to them, we will be able to significantly lower the number of infections within two weeks. This will allow the healthcare system to cope more smoothly in the coming weeks and months, and will help prevent the avoidable deaths of COVID-19 patients and help avoid another lockdown.

However, if we do not follow these recommendations, we are endangering the lives of our families, friends and strangers, and risking an economic and social crisis in Poland. In turn, this means our irresponsible actions today will leave our children and coming generations with an unenviable future.

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Sfinansowano ze środków Ministerstwa Nauki i Szkolnictwa Wyższego na podstawie umowy nr 460/WCN/2019/1 z dnia 24.07.2019 r. stanowiących pomoc przyznaną w ramach programu „Wsparcie dla czasopism naukowych”

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