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CHEMISTRY OF RENEWABLES FOR SUSTAINABLE INDUSTRY

CHEMIA SUROWCÓW ODNAWIALNYCH DLA ZMODERNIZOWANEGO PRZEMYSŁU

***Summary**: Chemistry as a basic science and chemical industry as the principal provider of innovative materials for practically all sectors of contemporary economy, are in the center of unprecedented and revolutionary technical and social changes. These changes are necessary for mitigating climate disturbances and environmental deterioration, which threaten the future of humanity. In reference to recent international initiatives, like the UN Sustainable Development Goals, which underline the need for global economic changes based on recovery and circularity principles, we offer some comments on area of research and development. They are concerned with a mandatory transition from un-renewable fossil-based industries, like the petrochemical one, to new sources of energy and carbon-rich materials generated by novel processes compatible with zero GHG emission prospects.*

Our discussion is focused on biomass as a universal feedstock capable of satisfying global needs for energy as well as chemical materials from commodity to specialty. Secondly, principle drivers of innovation in the fields of new chemical reactions and processes, like catalysis are discussed. The discussion includes a recent strive for new functional materials in reference to all levels of their structural organization, from single atoms and surface phenomena, through nano-constructs and mesopore composites, to macro-molecular and supra-molecular aggregates. Finally, the need for a further development of innovation and feasibility assessment methods, based on green chemistry principles is mentioned. It is a condition for an efficient cooperation in biomass related international R&D projects, which have to be based on the harmonization of unified evaluation principles.

***Keywords**: Carbon dioxide industrial emissions and utilization; Biomass as chemical industry feedstock; Lignocellulose biomass conversions; Furan platform chemicals*

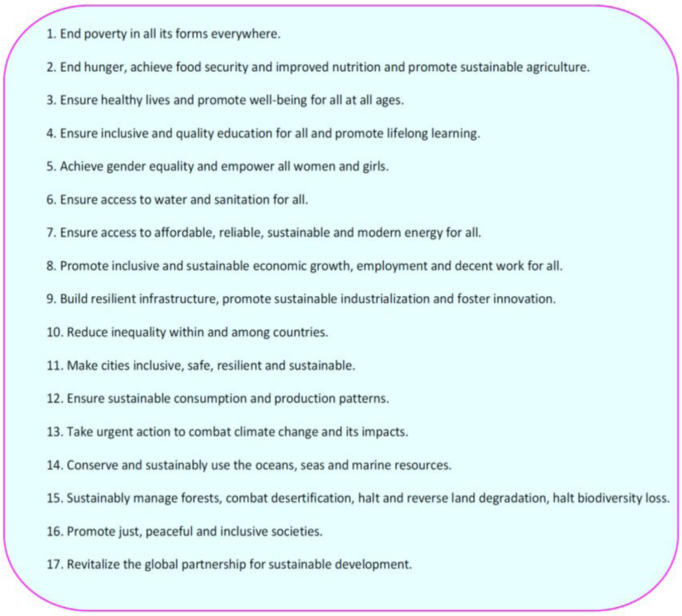
***Streszczenie**: Chemia, jedna z podstawowych nauk przyrodniczych oraz przemysł chemiczny, który zapewnia innowacyjne i nowoczesne materiały dla praktycznie wszystkich sektorów współczesnej gospodarki, znalazły się w centrum unikalnych i rewolucyjnych zmian ekonomicznych. Zmiany te, dotyczą nie tylko techniki i technologii, ale także mają znaczące skutki społeczne. Są one niezbędne w celu zminimalizowania dalszego pogarszania się klimatu oraz stanu naturalnego środowiska – zjawisk, które zagrażają przyszłości ludzkiego gatunku. Ostatnie inicjatywy, takie jak „UN Sustainable Development Goals", kładą nacisk na potrzebę globalnych przemian gospodarczych opartych o zasady regeneracji i cykliczności. W odniesieniu do tych inicjatyw i rozwoju znanych nam dziedzin chemii omawiamy obiecujące kierunki badań i rozwoju (R&D) związane z krótkoterminowymi cyklami organicznych związków węgla w kontekście transformacji od surowców nieodnawialnych (paliwa kopalne), do ekonomii nowych źródeł energii oraz materiałów organicznych, wytworzonych przez nowe procesy zgodne z wymaganiem zerowej emisji gazów cieplarnianych.*

Nasza dyskusja kładzie nacisk na biomasę jako uniwersalny surowiec, zaspokajający globalne potrzeby energetyczne oraz będący źródłem wszelkiego rodzaju produktów chemicznych. Ponadto, artykuł zawiera rozważania na temat podstawowych czynników innowacyjnych w zakresie nowych procesów i reakcji chemicznych, włącznie z nowymi katalizatorami. Do omawianych problemów i zjawisk należą próby wytwarzania nowych materiałów z uwzględnieniem różnych poziomów organizacji strukturalnej od pojedyńczych atomów, poprzez nanokonstrukty i mezokompozyty aż do agregatów makro i supra-molekularnych. W końcu, niezbędność dalszego postepu innowacyjnego oraz metod oceny wykonalności, wynikające z reguł zielonej chemii są także wspomniane. Jest to warunek konieczny do osiągnięcia skutecznej współpracy w zakresie miedzynarodowych projektow badawczych (R&D), które muszą bazować na harmonizacji ujednoliconych zasad oceny.

***Słowa kluczowe**: Przemysłowe emisje i utylizacja dwutlenku węgla, Biomasa jako surowiec dla przemysłu chemicznego, Przemiany biomasy lignocelulozowej, Chemikalia platformy furanu*

Introduction

The idea of rational management of earth material resources, which are finite, is not new [1–4]. Nevertheless, a massive social interest in closely related matters as preservation of environment and stabilization of climatic changes has become noticeable as a global force only recently, after a long series of appeals voiced through international expert gatherings (Stockholm 1972; Kioto 1997; Rio de Janeiro 1992 and 2012; Paris 2015 and 2021, Glasgow 2021). A recent initiative of the UN, popularized as sustainable development goals (SDG) has a form of manifesto, indicating 17 basic goals (accompanied by a list of 169 more specific targets and more than 300 indicators), which need to be achieved in near future in order to secure further development of human civilization in time of overpopulation and critical depletion of fossil resources of energy, fuels and chemicals. (Fig. 1; Fig. 2). [5–8] The EU follows with similar directives and recent program known as European Green Deal (EU Climate Target Plan 2030), which is focused on radical reduction of the atmospheric content of greenhouse effect gases (GHG), switch of industrial sectors to sustainable development mode and adapting it to the circular economy (CE) and bioeconomy BE) principles [9–16]. It is believed, although not without reservations, that these measures should secure a safety margin of global increase in average temperature and desirable climatic stabilization, but there is already a considerable amount of controversy concerning detailed means required for achievement of SDG [17, 18].



1. End poverty in all its forms everywhere.
2. End hunger, achieve food security and improved nutrition and promote sustainable agriculture.
3. Ensure healthy lives and promote well-being for all at all ages.
4. Ensure inclusive and quality education for all and promote lifelong learning.
5. Achieve gender equality and empower all women and girls.
6. Ensure access to water and sanitation for all.
7. Ensure access to affordable, reliable, sustainable and modern energy for all.
8. Promote inclusive and sustainable economic growth, employment and decent work for all.
9. Build resilient infrastructure, promote sustainable industrialization and foster innovation.
10. Reduce inequality within and among countries.
11. Make cities inclusive, safe, resilient and sustainable.
12. Ensure sustainable consumption and production patterns.
13. Take urgent action to combat climate change and its impacts.
14. Conserve and sustainably use the oceans, seas and marine resources.
15. Sustainably manage forests, combat desertification, halt and reverse land degradation, halt biodiversity loss.
16. Promote just, peaceful and inclusive societies.
17. Revitalize the global partnership for sustainable development.

Fig. 1. Basic sustainable development goals listed by the UN

It is generally agreed that present climatic crisis is produced by the increasing content of GHG in the atmosphere, with a decisive input coming from carbon dioxide. It has in turn led to a significant redistribution of preindustrially existing carbon pools. A recent report of the Intergovernmental Panel on Climate Change [19] on the physical science basis of climate change leaves no shade of a doubt that tiny changes in the atmospheric GHG content, resulting from industrial activities, will bring about irreversible and catastrophic changes if not properly attended [20–23]. The present estimate of elemental carbon stock include 800 Gt (atmosphere); 40 000 Gt (hydrosphere); 2 500 Gt (biosphere); and 65 mln Gt (lithosphere ; including 4 000 Gt of high energy fossil materials such as coal oil and natural gas).

Although anthroposphere (reduced carbon stored in fuels, polymers, etc.) amounts to only ca. 2–3 Gt and anthropogenic CO_2 emissions are of the order of 10 Gt per year, they manage to disturb the steady state global carbon balance and cause dangerous average temperature increase. Naturally, a close look at biosphere and biomass circulation is needed in order to mitigate effectively detrimental atmospheric changes induced by the excessive GHG presence. Every organic substance which derived from photosynthetic process, directly or indirectly, can be considered biomass, and a part of biological carbon cycles which are very short, in geological time scale. Estimates of the global amount of organic carbon are approximate since diverse and heterogeneous materials have to be assessed. Although mass units are customarily applied for the purpose, the energy equivalents are also frequently present in statistical data. It is assumed that earth biosphere (all kingdoms of life) consists of ca 550 Gt of carbon (Gt C), of which terrestrial plants are biggest part (ca. 450 Gt C), followed by bacteria and archea (70 and 7 Gt C respectively), marine biota (6 Gt C) and land animals (2 Gt C). The biosphere has 33 000 EJ energetic potential capacity, equal to ca 80 world annual energy consumption equivalents [24, 25].

Presently, the net-zero-CO_2 emission state needs to be introduced as a necessary measure to save the earth biodiversity and protect the environment capacity to support human population of present size. Obviously, the goals of programs defined in the documents and treaties quoted at the beginning of the paragraph, like 55% global GHG emission reduction before year 2030, can not be achieved by pursuing economy based on nonrenewable resources of energy and materials. Our sustainable future

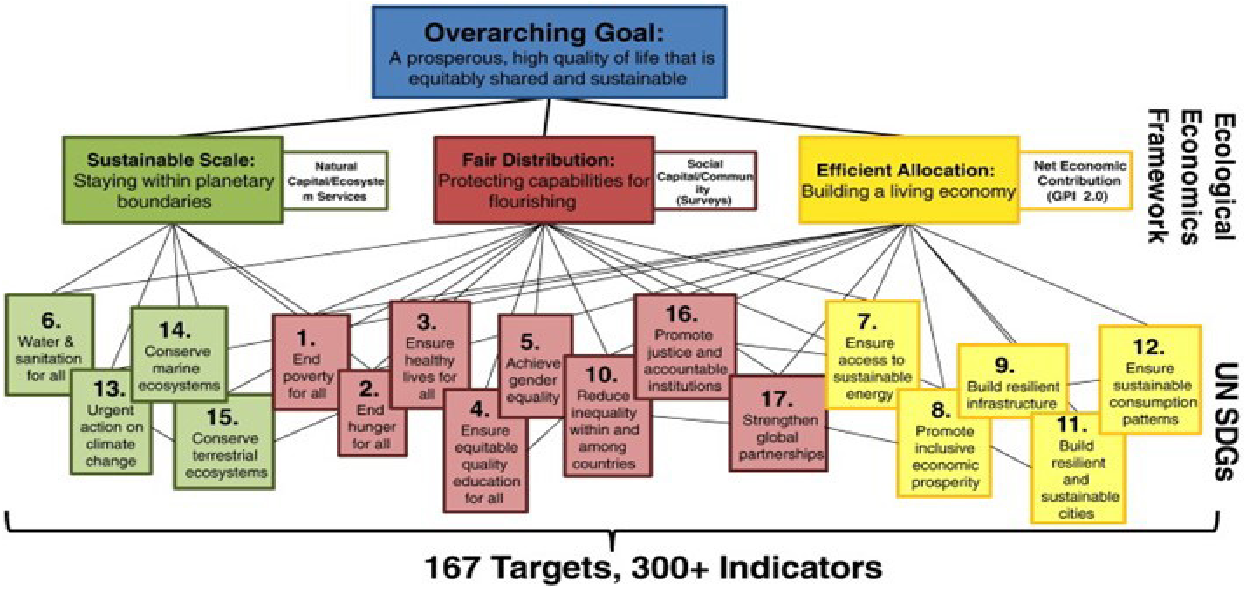


Fig. 2 Graphic network of the UN's proposed targets

requires immediate implementation of radical reduction of CO_2 emissions. Assuming more or less stable human population size, it can be practically achieved only in two ways: by capture of industrial waste carbon for immediate utilization (CCU) or for effective storage (CCS) [26–28]. Both options are already technically validated but remain the matter of vigorous dispute since they require different immediate resources, some long term investments and considerable energy inputs. Also, their short term and strategic consequences can vary greatly. While sharing an interest for carbon capture as the immediate climatic crisis remedy, we should be more concerned with strategic perspectives of chemical industry based on de-fossilized feedstock and clean energy, preferably solar, truly renewable in astronomical scale (the sun provide more than 10^5 TW).

Captured carbon dioxide of industrial (or atmospheric) origin can be a reasonable starting material for low molecular weight commodity chemicals, like syngas, methanol or ethylene (provided adequate supply of green hydrogen is secured), but is somewhat less viable as the requirement for carbon chain length (and structural complexity) of the end product increases. Therefore, this presentation is focused on sustainable chemistry based on lignocellulosic biomass (LCB), which is a renewable feedstock, available in considerable variety of forms, of collective mass suitable for an array of processes aggregated under umbrella term – biorefining [29–30]. The following short review of biorefineries utility for perspective platform industrial chemicals suitable for circular economy (CE) is preceded by short outlook of the present day chemical industry, which contributes (in form of energy, fuels and materials) to nearly every marketable products used in our everyday life. For example, industrial sectors operating chemical processes deliver very wide array of materials ranging in scale from billion tons per annum (steel, cement and other construction materials), through Mt/y commodities (petrochemicals, ammonia, fuels, plastics, processed agricultural crops) to specialty chemicals (solvents, monomers, catalysts etc.), and pharmaceuticals, which are applied in very small doses but their high market value and importance for healthcare makes them significant part of economy. In the last decade the value of sold chemicals increased from ca. 500 bln Euro in 2010 to 657 bln in 2019 and 649 bln in 2020 [Eurostat 2021]. Versatility of the chemical industry products is stunning. European Chemical Agency (ECHA) lists over 106 000 commercially manufactured chemicals, while globally there are at least 350 thousand chemical products on the markets (including some mixtures and compositions), which creates paramount complications with their technical specifications, life cycle assessments, as well as toxicological and environmental safety evaluation, and corresponding regulations [31, 32]. While experimental chemistry is principally based on measurements and their interpretations, we owe an extension of quantitative perspective of industrial chemistry towards economical and social consequences of its activity to green chemistry movement which introduced atom economy calculations, followed up by techno-economical assessment (TEA) and product life cycle analysis (LCA) as principal tools of evaluation [33, 34].

For decades, the chemical industry in Poland (as well as its sub-sectors) has been a subject of experts' debates addressing permanent systemic problems. However, the urgent need for radical and rapid reaction to pressures exerted by the global climatic crisis was brought up as a topic of wider social dispute only recently [21, 23, 35, 36]. Despite of persistent crisis resulting from preserving the state subsidized coal economy, there are continuous sound attempts, carried out by Polish Chamber of Chemical Industry (PIPC; *www.pipc.org.pl*) to discuss problems (and also perspectives) of the local chemical sector enterprises in the wider context of the EU Council policy and EU Chemical Chamber (cefic; *www.cefic.org*) initiatives and programs. PIPC publishes annual reports on sectorial productions and markets and presents local initiatives compatible with European policy of decarbonization, renewable energy, industrial recycling and sustainable economy, securing forum for innovating initiatives, scientific as well as industrial.

CE (the economy which is environmentally and materially renewable) is based on a stakeholders (society, government, business enterprise) point of view, considering feature network of: resource availability and management, speed of waste generation and increase in environmental risk, product design and LCA, technical efficiency of employed processes, and economic benefits through circular rather than linear exploitation of resources. A detailed discussion of the topics involved leads to a conclusion that such fundamental transformation of the global economy as "decarbonization" and ban on the use of fossil resources for energy, fuel and chemical production, could not be achieved without the massive innovation in literally every industrial segment. This, in turn, cannot be created without the involvement of basic science. Chemistry is a perfect example of basic science of fundamental importance to applications such as chemical engineering, material sciences and chemical industry, which delivers most of the commodities supporting contemporary technical civilization and everyday life of the planet population. Frequently called "central science" for its capability of interpreting transformation of matter on the atomic and molecular level [37], chemistry as an academic enterprise has attained admirable level of perfection in assembly of the most complicated molecules, natural and designed by inventive minds, in numbers running over hundreds of millions of individual chemical entities [38]. In our opinion, the key role of chemistry in general and chemical synthesis in particular, in the new sustainable technological future has not been sufficiently discussed and stressed as a necessary and complementary component of search for renewable energy sources.

The need for replacing petrochemical processes (employing non-renewable hydrocarbon as substrates) used thus far for making indispensable chemicals (basic, intermediate, polymeric, agrochemical, pharmaceutical, etc.) with renewable (biomass; LCB) resources is necessary and urgent. Therefore, we would like to present shortly the potential of modern chemical synthesis, based on chemo- and bio- catalyses in transformation of renewable LCB into chemicals through assorted dedicated processes, focusing on innovations concerning basic chemistry as well as well as process design and engineering [39, 40]. Since radically novel chemical industry needs to be established in place of traditionally practiced transformations of oil, natural gas, and coal, the question of science literacy and in particular chemical education comes to mind as an important factor shaping attitudes of today policy makers and future social forces. To this end we have elected to precede the biorefinery discussion with reflections on chemistry image in general and its evolution in direction of sustainability supportive force through propagation of the green chemistry principles. Finally, we would like to discuss some novel methodical openings in organic synthesis, which offer new perspectives for application in biorefinery chemistry, in respect to commodity chemicals, as well as to high value intermediates, new drug leads and pharmaceuticals. Apart from new applications in catalysis, a trend to fortify existing chemical knowledge with AI methods, such as large database mining, extensive algorithm operation applications, neural networks and machine learning systems will be mentioned as tools, which enhance functionality of synthetic methodology generated through collecting experimental laboratory data of generations of traditional chemists.

Carbon dioxide dual label: greenhouse gas and/or valuable commodity?

Our environment, including carbon cycles and climate changes, is studied on the planetary scale, within Earth System Science. The studies have accumulated a large amount of current and historical data describing accurately trends like a steady growth of the CO_2 atmospheric content, which correlates with its industrial emissions [16, 20, 23, 25]. The capacity of biosphere for photosynthetic fixation of atmospheric CO_2 is huge as evidenced by global biomass generation which is in excess of 10^9 t/y and steady photosynthetic production of oxygen at 290 000 Tg/y. Carbon, which is the essential element of life, makes up only 0.03 % by weight of our planet but its partition between reservoirs and sinks is very uneven, in favor of geological deposits. Indeed, 99.95% of carbon is located in crust and mantle, 0.049% is dissolved inorganic carbon, while terrestrial and marine biospheres combined contain only tiny 0.00064%. Incidentally, the same fraction: 0.00064% is present among atmospheric trace gases (like CO_2 and CH_4) [41, 42]. During the recent two centuries or so atmospheric CO_2 levels rose from preindustrial 180 to over 400 ppm. Consequently, a continuous rise of average temperature (over 2°C global average from the preindustrial period) has been observed, threatening climate stability, land and water resources, and eventually sustenance of the human race [21, 22]. Although human made carbon dioxide fraction of the carbon cycle (37.1 Gt in 2018, projected to increase annually by 10% until 2040) seems small, it is by no means insignificant. Consequently, programs that enable achieving zero GHG emission economy in a foreseeable period of time are of critical importance [8-10]. An apparent priority of the atmospheric carbon dioxide sequestration has led to considerable amounts of research. Initially, it was classified as carbon capture and storage (CCS; CO_2 capture exercised as: absorption, adsorption or membrane technology process), and subsequently as more prospective carbon capture and utilization (CCU) [26, 27]. In fact CO_2 capturing at a source of emissions, transportation, compression to supercritical condition, and geological storage (primary form of CCS) is a considerable technical problem in itself, not to mention prospective containment safety issues.

Alternatively, sorbent technologies can be applied for storage, e.g. mineralization with alkaline materials or reversible salt formation with monomethanolamine as the most common dedicated solvent. Some direct utilization may include soft drink carbonization; food refrigeration and storage; welding protection; fire extinguishers, etc. Physical sorption seems more suitable for small scale applications. However, new solutions are constantly developed - graphene-type materials are promising, with current capacity of ca. 0.07 mol/g (it corresponds to over 3 g of CO_2 per g of ther material) and other types of molecular sieves (e.g. MOFs, zeolites) may also be applied for storage [43, 44]. Considerable part of CO_2 industrial applications derives from its particular physicochemical properties which makes it suitable as heat transfer medium, supercritical fluid (sc CO_2), extraction or reaction solvent, etc.

CCU prospects in the chemical industry span from various forms of chemical reduction, powered by thermal, electrical or solar energy to biochemical fixation (photosynthesis, earlier called assimilation) performed by organisms like cyanobacteria, algae or higher plants [45, 46]. Interestingly, a study evaluating 14 selected technologies of CO_2 utilization was recently offered by Polish scientists in the coal power plant in Jaworzno. That critical CCU implementation study covered technical as well as economic analysis of the particular medium size facility placed in the industrial region, in relation to the European Emission Trading Scheme system (EU ETS) and local reform plans. The study indicated a strong influence of non-technical issues on the results of final assessment [47].

Before discussing the possible reactions of CO_2 we must note that thermodynamically it is an exceptionally stable compound. It is due to the presence of two carbon-oxygen double bonds in a very small molecule. Elemental nitrogen consists of similarly thermodynamically very stable molecules. The synthesis of ammonia from nitrogen (and hydrogen) is rightly considered one of the greatest accomplishments of chemical engineering and industry. Transforming CO_2 into useful chemicals is an equally difficult task. It demands that cheap (hopefully solar) energy is available. Note also that two stages of the utilization of CO_2 are possible: one or both C=O bonds can be broken.

It seems that a short review of CO_2 chemistry and remediation should begin with a reminder of its basic redox properties. The single electron reduction, resulting in the disturbance of molecular geometry from linear, non-charged molecule to the bent anion-radical has the standard potential of + 1.90 V and is practically of no use for chemical transformations, except in the semiconductor catalysis. Multi-electron proton assisted reductions are observed in a more favorable range of electrochemical potential. Consequently, they found appropriate catalytic enhancement conditions and wide practical applications [17; 48–50]. The potentials of applicable processes are:

$CO_2 + 2H+ + 2e^- \rightarrow CO + H_2O \quad E^0 = -0.53\ V$
$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- \quad E = -0.93\ V$
$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O \quad E = -0.07\ V$
$CO_2 + 3H_2O + 4e^- \rightarrow CH_2O + 4OH^- \quad E = -0.90\ V$
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \quad E^0 = -0.61\ V$
$CO_2 + H_2O + 2e^- \rightarrow HCO_2^- + OH^- \quad E = -1.08\ V$
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^0 = -0.38\ V$
$CO_2 + 5H_2O + 6e^- \rightarrow CH_3OH + 6OH^- \quad E = -0.81\ V$
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad E = +0.17\ V$
$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^- \quad E = -0.66\ V$

where values of redox potential quoted refer to either equilibrium potential (E^0) or standard equilibrium potential (E) for aqueous solutions.

In fact, each entry from the above list of conversion of CO_2 to high energy products corresponds to a bunch of experimental procedures and variously designed technical processes. They may differ in employed catalysts, molecular mechanisms, modes of electron transfer, overall efficiency, etc. For example, at first complexes of the noble metals (Pd, Ru, Pt) were favored as hetero- and homogeneous catalysts for CO_2 hydrogenation, while recently there is more focus on easily available complexes of transition metals (Fe, Co, Ni, Cu, Mn) [51]. Thus, although chemically stable and useless as an immediate energy source, the notorious GHG – carbon dioxide, can be considered as a feedstock of renewable carbon. Note, however, that carbon dioxide utilization in a traditional industrial mode would require a reduction agent (e.g. hydrogen) and energy, which according to principles of de-fossilization and CE, must also be free from fossil C-trace [52, 53].

Traditional industrial applications of carbon oxides, such as Sabatier methanation, Kolbe carboxylation of phenols, and Fisher-Tropsch synthesis (FTS) of hydrocarbon fuels are still utilized chemical technologies [51]. The discovery of natural gas (composed mainly of methane) and coal oxidative conversion to syngas (consisting of CO/H_2 mixture) provided a novel fuel, and also a reducing agent suitable for many synthetic applications. The FTS process for liquid fuel manufacturing was described and patented in 1920-ies. This Fe or Co catalyzed moderately high temperature (160–200°C) and pressure (10–40 bar) process was developed to 0.6 mln t/a capacity in the 2nd world war time Germany [54, 55]. Another commodities made from carbon dioxide are: urea - 170 mln tons and methanol - 65 mln tons per annum).

The current R&D on CO_2 reduction reactions (CRR) turned to low temperature variants and biomass-based feedstock, looking for scale and end product optimization under such cost determining factors as local electric power and hydrogen prices. Regardless of the obvious and unsolved need for green energy in the post-petrochemical era, chemistry of renewable low molecular weight carbon synthons has advanced considerably, mainly due to a remarkable progress in both, chemical and enzymatic catalysis. Thus CO_2 ability to act as a mild oxidative and dehydrogenative agent under suitable catalysis has been exploited for syngas production and in various hydrocarbon reforming processes [56, 57]. Examples include already mentioned reduction of CO_2 to carbon monoxide, carbonate, methanol and follow up MOL (methanol to olefin) family of processes, production of methane, ethylene, etc [58, 59]. A large majority of these reduction reactions are highly endothermic and require much energy. Nevertheless, such reactions as organic carbonate (or carbamate) formation can be completed at much milder conditions. Presently, overall inorganic carbonates market is twice as big as that of organic products, by volume.

The R&D on chemical conversions of CO_2 enjoys a continuous and growing interest. When split into thermochemical hydrogenation, electrochemical reduction, and photochemical reduction categories, the number of publications revealed by bibliometric analysis in the last few years topped 1000 per year in the first two groups. Attention to photochemical reduction is much weaker, but it is exactly the category likely to bring a breakthrough results by coupling synthetic biology constructs to visible light energy collectors [60, 61]. The three proposed mechanistic paths of CO_2 reductions are called: formaldehyde, carbene and glyoxal pathways. Each one is composed of chain of ionic and/or radical species leading to the ultimate reduction product – methane. The four intermediate reduction products are – carbon monoxide, formic acid, formaldehyde and methanol. The last compound deserves special attention as a commodity chemical of multiple applications, as well as a fuel candidate, hydrogen carrier, and precursor of solvents and monomeric substrates for biodegradable polymers. A variety of catalysts, heterogeneous and homogenous, are applicable to MeOH synthesis, from syngas as well as from CO_2 (following pioneering $ZnO–CrO_3$ catalyst operating in 320–450°C and 250–350 bar, commercialized by BASF), and also for its thermal reforming in which hydrogen can be recovered. It has been pointed out, in juxtaposition to the “hydrogen economy” proposal, that “methanol economy” is much safer and more efficient [62]. As a proof, the CRI demonstration facility was launched in Iceland, named George A. Olah Renewable Methanol Plant, with production capacity of 4000 t/y, which recycles ca 5600 t of CO_2 per annum.

Interestingly, methanol can also be obtained directly by catalytic oxidation of methane, another GHG threatening climate stability. For that purpose Mo and V based catalysts have been developed [63]. It is also worth mentioning that natural biocatalyst – enzyme methane monooxidase exists and can be expressed in suitable microorganisms for the whole cell biotransformation of industrial significance [63].

It has been postulated that algal biomass farming on land, using air enriched with CO_2 and solar energy can be used for synthesis of fuels or their precursors with higher efficiency than that accomplished at LCB biofarms. Another area of an increased interest is the production of formic acid (HCO_2H), easily obtainable from CO_2 by chemical, biocatalytic or electrochemical reduction, as a convenient, safe and efficient source of molecular hydrogen [64, 65]. The relevant processes are based on either decarboxylation/dehydrogenation or decarbonylation/dehydrogenation decomposition and are catalyzed by a variety of iridium and ruthenium complexes. Organocatalysis, microbial electrosynthesis (MES) and the use of acetogenic bacteria from genus *Clostridium*, which can produce alcohols and organic acids directly from CO_2 and H_2, are other currently pursued concepts [66, 67]. Natural photosynthesis, which efficiently produces ca 115 Gt of biomass from atmospheric CO_2 every year remains yet unattainable inspiration for an efficient human designed mimicking system. Although currently at least six different autotrophic carbon-fixing pathways are known [68], attempts to improve the key steps around the enzyme catalyzing condensation of ribulose 1,5-diphosphate with carbon dioxide (Rubisco) [71] by bioengineering are not particularly encouraging. It appears that CO_2 biosequestration with the help of algal farming (carried out on land unfit for agricultural production) is a viable solution, at least in short and medium term perspective. It is due to a very good biomass productivity and high yield of lipidic (oily) metabolites accumulation [45-46]. Biomass in not necessarily the most desirable product of the CO_2 biocatalytic conversion. Thus, while algal biomass resulting from CO_2 sequestration can be considered a suitable feedstock for biorefineries offering various biofuels, simpler photoautotrophic organisms – cyanobacteria – can produce such important value added chemicals (VAC) as β-hydroxybutyrate and its polymers (biodegradable PHB{poly(hydroxybutyrate}) directly from such inexpensive feedstocks as carbon dioxide or syngas [69].

Another example of industrial flue gases or various forms of syngas utilization for the so called cell factory carbon source (much cheaper than regular industrial bacterial fermentation carbon sources) is the production of an important industrial chemical: ethanol. It has been traditionally obtained from sugar rich materials (as sugar cane or fermentable starch crops). Recently, it became available from a variety of technical processes based on non-edible agricultural materials (e.g. LCB), including direct fermentation of syngas with the aid of *Clostridium* type bacteria, which deploy Wood-Ljungdahl reductive pathway called solventogenesis [70]. In a long run, green synthesis powered by solar light as the carbon-free energy, aided by either biocatalysis or chemical catalysis (or both) will end up as the target mode of biorefineries operation. [71, 72]. Also, a significant progress in genetic and metabolic engineering of microorganisms to suit bioproduction processes of assembling value added chemicals directly from CO_2 (or formate as C_1 equivalent) by acetogens like heterotrophic E. coli, achieved very recently [73] indicate a vast capability of yet untouched innovation areas based on metabolomics.

Biorefineries – essential part of modern economy

Higher forms of life on earth depend on metabolism of autotrophic organisms, which developed ability to use solar energy to split water into elements (H_2 and O_2) and utilize it as a hydrogen source for reductive assimilation of atmospheric carbon dioxide [24, 25, 60, 68, 71]. In the follow up biochemical cycle processes thousands of newly formed small molecules are gradually assembled in plant cells into bio-macromolecules, like proteins and nucleic acids, which we recognize as the essence of life. Plants, both growing, and beyond their vegetation cycles are classified as biomass and recognized for multiple applications, as food and energy sources, construction materials, etc. The technical civilization emerged couple of centuries ago from mastering extensive exploitation of fossilized biomass as a feedstock for energy and industry. However, modern ideas of sustainable development stress the urgent need for rational managements of the earth resources and their recovery and circulation [20–22].

One of the wanders of life, which happens to be available affordably in vast quantity and also renewable within annual solar cycle, is lignocellulosic biomass (LCB; agricultural or forestry materials and wastes are good examples of it). It is composed mainly of three biopolymers: cellulose (30–50 % by weight), hemicellulose 20–40 %) and lignin (15–25 %), interwoven into sturdy constructs, which render to plants their structural stability and environmental resistance. From the chemical standpoint, LCB basically consists of polysaccharides, containing hexoses (C6 monosaccharides like D-glucose, the monomer of cellulose) and pentoses (C5 monosaccharides, mainly xylose), which feature many structural and functional characteristics. They include susceptibility to fungal and bacterial degradation, often described as fermentation (a set of processes exploited for food processing and conservation from the outset of humanity). Sugars as part of organic matter attracted an interest of life scientists in many fields, developing into specialties like multi-branch carbohydrate chemistry omnipresent in biochemistry and medical sciences, glycobiology, organic chemistry of sugars, industrial carbohydrates, etc., all blossoming in the previous century. While traditional carbohydrate chemistry/biochemistry accumulated vast amount of scientific data concerning individual sugars, their chemistry, functions and possible applications, knowledge of the composite structural biopolymer – LCB, featuring considerable resistance to chemical and biological deconstruction, largely lagged behind advances of the mainstream sugar chemistry. The last decades, on the other hand have faced explosive development of interest in LCB as a prospective replacement of unrenewable fossil resources, under the banner of biorefineries [11, 12, 16, 29, 30, 74–78] (Among hundreds of relevant references, there are some excellent texts published in Polish [79, 80]).

There are various types of biorefineries, customarily recognized on the basis of the feedstock used, process applied and/or products manufactured. In general, the traditional application of biomass for conversion to energy, even if switched from burning to manufacture biogas or bio oil, is becoming obsolete with advance of new technologies, striving for value chain extension and selective products manufacturing [81–83]. Unlike isolated biopolymers: cellulose, hemicellulose pentosanes, and alkylaromatic lignin, which feature some specific chemical reactivity, their natural conglomerates classified as LCB are known for exceptional recalcitrance towards chemical reactants, as well as biocatalysts. Therefore, practically all types of LCB require some kind of pretreatment before basic biorefinering steps: depolymerization and further biocatalytic or chemical processing [84–86]. Commonly used treatments include: mechanical (grinding, milling, extrusion); physicochemical (steam explosion, ammonia fiber explosion, irradiation, microwave); chemical (alkali, acids, solvolysis, ionic liquids, inorganic catalysts, oxidation); biological (enzymes: cellulose, laccase, pectinase; microorganisms; fungi; bioengineered microorganisms) [87]. An established procedure of LCB pretreatment and fractionation, dedicated to dry high cellulose content biomass, known as Organosolv process, consist of thermal treatment of starting materials with low boiling aqueous alcohol, and a catalyst, in a series of precipitation/filtration operations which afford a water soluble fraction (containing sugars, furan derivatives and organic acids), organosolv lignin, and solid fraction of polysaccharides suitable for enzymatic hydrolysis [83].

Biorefinery industry started launching facilities in EU a decade ago, following new regulatory developments and EU R&D programs with over 80 bln euro funding. In 2017 there were 224 biorefineries operating in Europe, although only 43 so-called second generation, using LCB feedstock, while majority applied agricultural crops for bioethanol fermentation or used various wastes or residues [88]. There is no doubt that biorefineries are to play a major role in development of circular bioeconomy since their various models have already passed proof of principle points and started commercial operation [89]. Nevertheless, a lot of chemical innovation and advanced engineering is still required for design of facilities operating on carbon-free energy and providing advanced materials, like monomers for biodegradable polymers and platform chemicals, selectively.

As we have mentioned, biorefinery is rather flexible term, accommodating various feedstocks, processes and products, as long as renewable resources are valorized into products suitable for circular economy. From such point of view, much of carbon dioxide chemistry discussed above, can also be considered as a kind of biorefinery. Also, algae and cyanobacteria farming, initially developed for oleoproducts and biodiesel fuel, are recently treated more as microbial factories for a variety of secondary metabolites (carotenoids, fatty acids, chlorophyll, antioxidants, biopolymers) for applications as food, feed, nutraceuticals, and even pharmaceutical active substances [90]. The algal biorefinery concept seem to have considerable potential for further development for manufacturing structurally complex biologically active compounds for healthcare, under mild and environment friendly conditions.

Furan platform chemicals (FPC)

Much of the research in the biorefinery area has been focused on biofuels. From that standpoint, LCB as a biorefinary feedstock has a wrong elementary composition (too much oxygen, the proportion of oxygen to carbon is almost 1:1), which should be corrected by hydrogenation. Thus, LCB is a less attractive starting material for manufacturing fuels than hydrocarbons present in the crude oil. Also, carbohydrate chemists are not particularly excited about multiple deoxygenation, since it leads to a loss of chirality, which in natural products domain is a value in itself. On the other hand, using biomass as a substrate allows synthesizing fuels with very specific structures that can be better in terms of exhaust gases composition as compared with gasoline.

Carbohydrates are the main constituents of biomass and biorefineries aim at their conversion into high energy compounds of different chemical characteristic. Thus, at early stages of the process there is an unprecedented complexity of multifunctional substrate composition, which needs to be managed to the point of acceptable selectivity in manufacture of desired products. As LCB gets deconstructed in the initial stages of its processing, monosaccharides formed meet harsh and degrading environment, in which they undergo a variety of irreversible transformations leading in opposite directions: fragmentation into smaller molecules, and condensation/polymerization towards poorly characterized high molecular mass materials, called humins. Thus, a process design of suitable chemical (or biocatalytic) selectivity appears as the key issue in a refinery technology [32–34]. Since our paper is mainly concerned with material production of a new post-petrochemical industry, we decided to select one line of chemicals, FPC – furan platform chemicals, for an illustration of new short carbon cycle pathways, capable to satisfy the demand for industrial commodities within circular economy framework. Somewhat unexpectedly, the example of an industrial process in which agricultural waste is converted selectively into a useful multipurpose chemical of commercial value, has been operational for over a century and came into being as an invention out of economic needs [91-92]. As a consequence of first furfural (FUR) production, furan chemistry was born as an important chapter of heterocyclic compounds field [93, 94] but the idea of biomass as a chemical feedstock (apart from biotechnology) had to wait for its second chance until the climate crisis.

Furfural is a product of hemicellulose depolymerization-dehydration (C-5 sugar platform) and its extensive and versatile chemistry found many practical applications [93, 95-97]. It must be noted, however, that its C-6 analog, obtainable from hexoses (HMF; 5-hydroxymethylfurfural) has a much larger potential, particularly as a monomer of biodegradable functional polymers. It is because HMF is already bifunctional and its functional groups are conveniently differentiated, to allow for the generation of derivatives with easily controlled span of reactivity. Hundreds of compounds can be obtained from HMF by relatively simple chemical transformations and a small selection is presented on the figure below, to illustrate the possibility of ring and chain type variation in the design of future polyesters, polyamides, polyurethanes, polyacetals, etc. HMF like FUR was discovered in XIX century and both compounds are on DOE's top 10 list of biobased chemicals for industrial use but the commercialization of the more promising one (HMF) is still in the demonstration phase. It is estimated that at present bioerfinery HMF and array of its derivatives would cost three time as much as the same products obtained from petrochemicals [98, 99]. Nevertheless, R & D studies on HMF production, both from model and real biomass feedstock remain a hot research area as evidenced by an avalanche of current publications [100-105]. Naturally, it is expected that the cost of HMF will dramatically drop with rapidly increasing production.

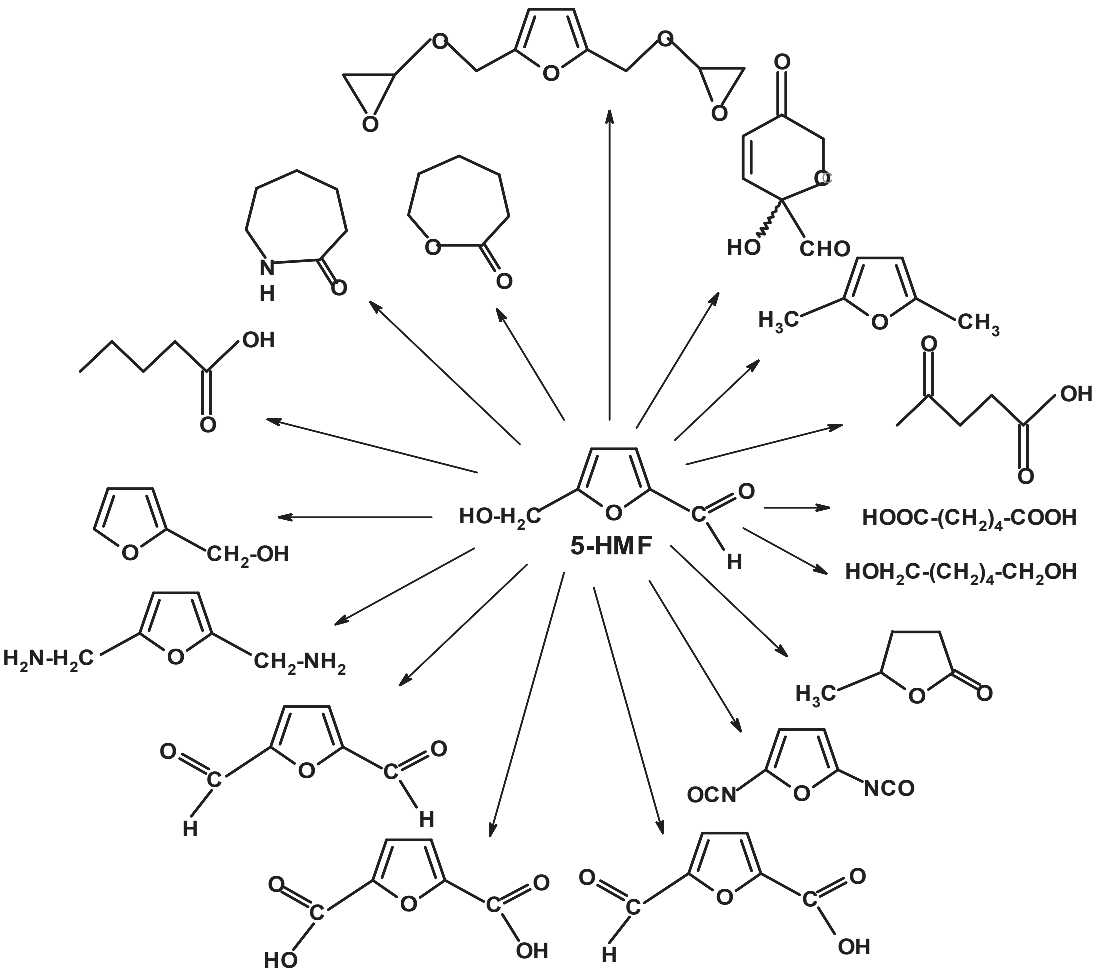


Fig. 3. Selection of simple derivatives of 5-hydroxymethylfurfural designed for further development as fine and specialty chemicals

One of the most promising derivatives of HMF, allegedly close to commercialization, is its oxidation product: 2,5-furandicarboxylic acid (FDCA). It can be considered as a bifunctional symmetric carboxylic acid, prospective monomer for polyester, polyamide, polyurethane biodegradable plastics, and a good replacement for such industrial chemicals as maleic, succinic, and terephtalic acids. As can be expected, several variants of chemical synthetic routes for FDCA, from FUR or HMF already exist [106–110], but translation from demonstration facilities to commercial manufacture is withheld because TEA and LCA assessments are not convincing [111]. Meanwhile, new opportunities based on biocatalytic transformations are maturating to enter the race for future monomer markets [112–114]. Thus, FPCs are essential for sorting out crucial issues of future chemical industry sustainability: origin of commodities and their respective life cycles specification [115], and notorious environmental pollution with polymers resistant to biodegradation [116]. The first issue can be addressed based on analytical methods suitable for LCA [117, 118], in particular Accelator Mass Spectrometry (AMS), designed for carbon dating through precise measurements of the carbon isotope ratio [119]. The environmental plastic pollution problem, on the other hand, has grown to catastrophic proportion. It has been estimated that since the mass production of synthetic polymers started 1950, ca. 6.3 Bln t of plastic waste was generated to 2015. In 2019 annual production of plastics reached 370 M t and it is still growing. Plastic recycling is low and majority of plastic wastes end up in landfills and oceans. While we have proper tools to diagnose the situation, there is still no clear answer how it could be remediated and what should be the role of biobased plastics in the process [120–122].

Conclusions

A decade ago an important exchange of opinions concerning the future of chemical synthesis as a provider of commodities and materials supporting technical development, took place between distinguished scientists representing different methodological inclinations [123]. While J.D. Keasling of UC Berkeley enthusiastically presented a growing potential of engineered microorganisms for biotechnological synthesis of chemicals, A. Mendoza and P.S. Baran from The Scripps Research Institute distinguished between synthetic biology as the way to obtain some extremely complex natural products, from more traditional chemical synthesis which excelled in satisfying the needs of industrial chemistry for circa two centuries. Perhaps not surprisingly, the current view of the necessary fundamental transformation of industrial world into sustainable bioeconomy, carries two important messages concerning origin of energy and materials required to support technical civilization:

- the rational management of the anthropogenic input of GHGs into natural carbon cycles is a critical condition of survival; and
- all bioresources, including synthetic biology and metabolic engineering have to be mobilized for the purpose, in harmony with support from chemical synthesis, both traditional and advanced through the most recent research on design of new materials (and nanoconstructs) as molecular catalysts, and support for metal catalysts.

In particular, the progress in coupling photochemically induced charge separation in a water molecule to the electrochemical (or biocatalytical) processing of the energy and basic feedstock (hydrogen), which can be casually described as artificial (or technical) photosynthesis, will practically determine the pace of the transition to bio-economy, which critically needs clean renewable energy and renewable carbon materials from biomass. Apparently, there is still no natural economic incentive for a new platform chemistries based on catalytic biomass (LCB) conversion, in the real world of coal, gas and oil markets. There is a substantial measure of good will, however, included in international agreements and treaties on climate and CE. It makes possible implementation of the most promising processes in experimental development, demonstrational, and commercialization phases, which have passed technical feasibility assessments.

The idea of sustainable economy has to be moved forward by social understanding and consent, as well as by international cooperation and ample support from intergovernmental programs. From the technical point of view, there is no doubt that with the help of innovation amassed in the first two decades of 21st century, considerable advances in synthetic biology, nanotechnology, IT, chemo- and bio-catalysis and vast renewable resources of biomass can be rationally managed. It is necessary for supporting the transition to bio-economy, and halting the scenario of irreversible global warming. We are aware of an extremely complicated environment of political antagonisms, economic inequality, environmental crisis, pandemic health problems, etc., according to already signed international agreements and treaties. Nevertheless, the transition from fossil to renewable resources is unavoidable. It has to be stressed that it is a multidimensional mega-project of unprecedented dimensions, in which local and national initiatives should be united under the SDG and CE banners. That would require, apart from massive economic support, large amount of scientific and technical innovation, generated in considerable proportion in international cooperation projects, organized within the system of grant competitions. Obviously, such system will require harmonized and precise criteria of innovation, to evaluate and select prospective projects from plethora of similar proposals. Such a goal concerning biorefineries and bioeconomy seems even harder than in the case of evaluating R&D proposals within petrochemical realm, which developed already adequate evaluation standards fitting generally adopted Oslo Manual [124]. In the case of biorefineries, where TEA and LCA are based on sets of local parameters, the innovation assessment would refer to a process functioning under specific conditions, which may defy objectivity criteria. Naturally, all above mentioned elements of change need also solid support from sound scientific education free from any political bias. Therefore, it may be concluded that the present, rather limited participation level of bioeconomy in the global industry may hamper acceleration of much needed bioeconomic innovation, for lack of sufficient tools and instruments supporting the harmonized and efficient R&D effort [125].

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