

CATALYTIC METHODS FOR PROCESSING CARBON DIOXIDE FROM COAL-FIRED GENERATION INTO USEFUL PRODUCTS

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COAL GENERATION IN THE ENERGY CONSUMPTION STRUCTURE AND CO₂ EMISSIONS

Nowadays we face the situation when the effects of global warming are rapidly increasing, and the search for solutions goes beyond a simple technological problem [1]. We are in need of more integrated solutions connecting various areas and, as a result, bringing about a change in the patterns of life, thus ensuring the future of the planet and a sustainable development of society.

The new approach has led, for example, to the situation when CO₂, which is one of the main greenhouse gases, is no longer considered a waste but serves as a raw material for obtaining a significant range of the value-added products. This explains the renewed interest in the CO₂ conversion reactions that before now were used in industrial processes for processing only relatively small amounts of the above-mentioned compound. At present, there is no large-scale production allowing industrial processes without CO₂ emission. The reason is dependence, in most cases, of the economic viability of CO₂ conversion reactions on sustainable supply of H₂.

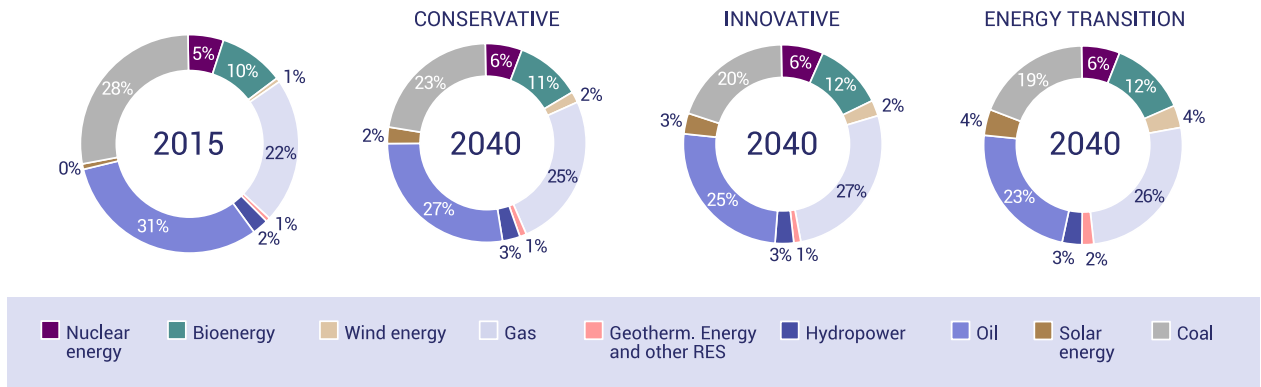
Industrialisation and population growth resulted in a sharp increase of global energy consumption, and anthropogenic CO₂ emissions increased

quickly because now fossil fuels are the main consumed energy resources. A steady rise of CO₂ concentration in the atmosphere leads to global warming and a number of environmental problems. Average global temperatures have risen by 0.8°C over the past 70 years [1]. The Paris Agreement is one of the international efforts made to reduce CO₂ emissions. At the same time, many studies have focused not only on development and application of the renewable energy sources as a means for reduction of dependence on fossil fuels [2] but also on technologies for CO₂ capturing and utilising.

Fossil fuels are the main source of energy resources and carbon dioxide emissions. The world's daily consumption of coal is ~22 million tons, oil is ~12 million tons and natural gas ~10 billion m³ [3]. Human activities result in about 34 billion tons of CO₂ annual emission into the atmosphere, almost 80% of which comes directly from fossil fuels.

Coal, oil and gas are expected to remain dominant in the global energy consumption in the coming decades. There is a predicted rise of contribution made by non-fuel (carbon-free) energy sources, but it will not exceed 30% (Fig. 1).

FIGURE 1. The structure of world's primary energy consumption by fuel type in 2015 and 2040 according to various scenarios of energy development [4].



Coal has been one of the cheapest and affordable sources of energy for many decades, and it will remain as such in the near future [4]. Currently, the share of coal-fired generation in the installed capacity of power plants in Russia is about 22% (56.6 GW). The share of coal generation reaches 65% in the Siberian Federal District and 93% - in the Far Eastern Federal District [5]. Russia ranks 13 in the world in terms of electricity generation by

coal-fired thermal power plants, behind China, India, the USA, the EU, and other states with energy systems based on coal generation [6].

The heating value of coal depends on its composition; it is ~30 MJ/kg for bituminous coal. As it is with combustion of any carbon-containing fuel, coal combustion produces a significant amount of carbon dioxide - 3.7 t of CO₂ per 1 t of C.

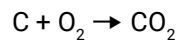


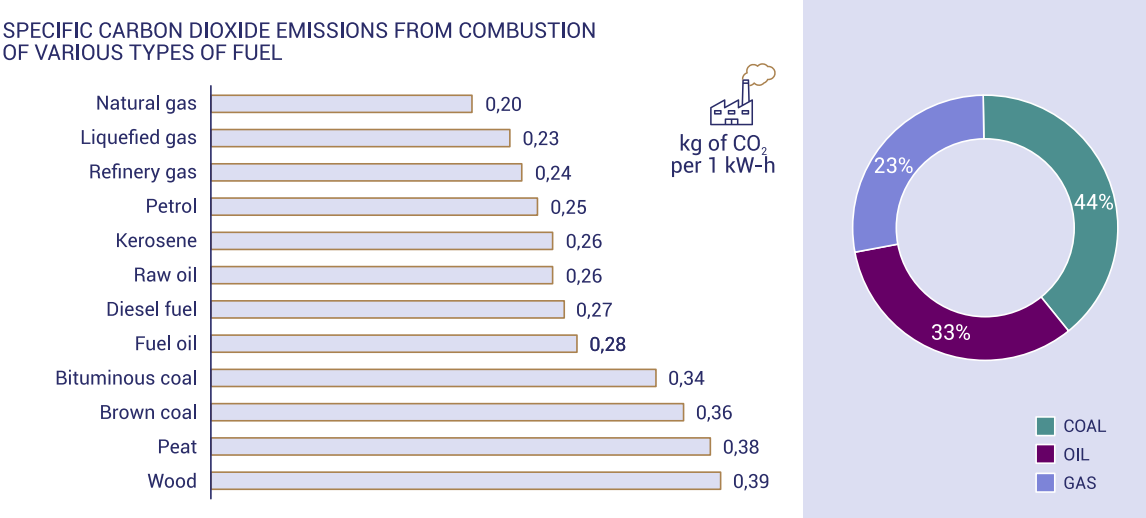
Table 1 presents data on the specific amount of CO₂ for various grades of coal without taking into account the heat loss during combustion, which can reach 55–75%. As we can see, the rise

of carbon content in fuel raises carbon intensity of the generated power. Compared to other fuels, coal is distinguished by higher emissions of CO₂ (Fig. 2).

TABLE 1. Specific CO₂ emissions from combustion of various coal grades. According to [7].

Fuel	Specific carbon content in fuel, kg of C per kg of fuel	Specific energy content in fuel, kW·h/kg	Specific CO ₂ emission	
			kg of CO ₂ per 1 kg of fuel	kg of CO ₂ per 1 kW·h
Anthracite	0.92	9.0	3.37	0.37
Bituminous coal	0.65	8.4	2.38	0.28
Brown coal	0.30	3.9	1.10	0.28

FIGURE 2. BContribution of the type of fuel to CO₂ emissions, and the amount of CO₂ emitted per 1 kWh of electricity obtained from combustion of various types of fuel [8].



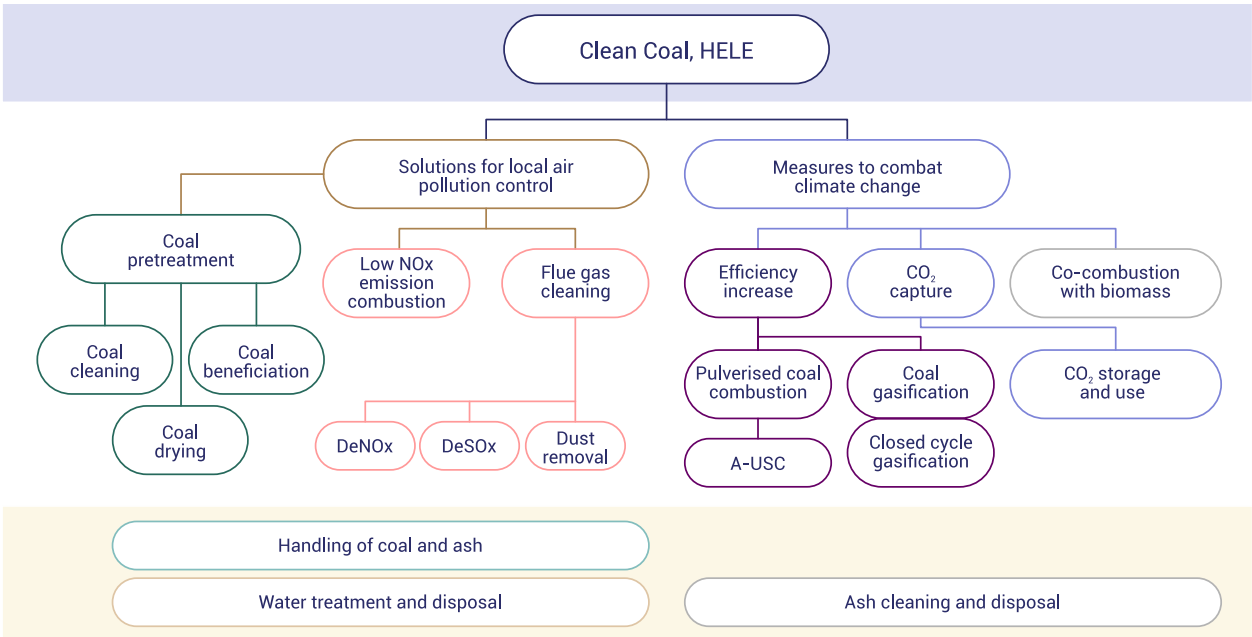
As of 2019, Russia is responsible for 4.71% of greenhouse gas emissions, after China (30.34%), the USA (13.43%), the EU27 + the UK (8.69%) and India (6.83%) [9].

In total emissions from 1850 to 2007, the top countries are as follows: 1. The USA: 28.8%, 2. China: 9.0%, 3. Russia: 8.0%, 4. Germany: 6.9%, 5. UK: 5.8%, 6 Japan: 3.9%, 7. France: 2.8%, 8. India: 2.4%, 9. Canada: 2.2% and 10. Ukraine: 2.2% [10].

To reduce harmful emissions into the atmosphere, almost all countries with the developed economies and technologies have set the task

of coal gradual reduction in the energy balance. To raise efficiency and environmental friendliness of coal-fired generation, the technologies known as Clean Coal or High Efficiency Low Emissions (HELE) have been implemented [6]. They include technological solutions to suppress pollutant emissions and purify flue gases by raising the quality of burned coal, using the nitrogen, desulphurisation and ash filters as well as a set of measures to combat climate change by increasing the efficiency of coal generation, capturing carbon dioxide and joint combustion with biomass (Fig. 3).

FIGURE 3. Technologies Clean Coal or HELE (High Efficiency Low Emissions) [6].

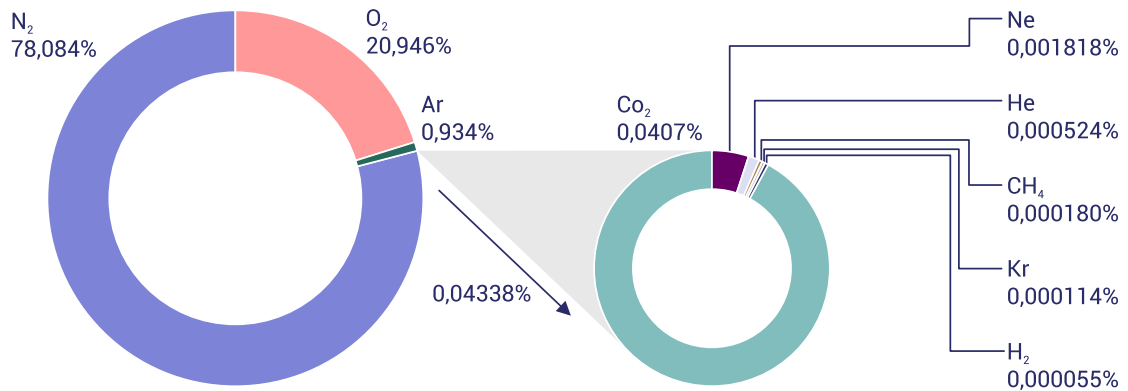


GREENHOUSE EFFECT AND CO₂

Carbon dioxide belongs to greenhouse gases (H₂O, CO₂, CH₄, N₂O and O₃) playing a significant role in the Earth's heat balance

and the greenhouse effect formation (Fig. 4) although they make up a small part of the atmosphere.

FIGURE 4. Dry air chemical composition [11]. The water content in the atmosphere (in the form of water vapour) ranges from 0.2 to 2.5 vol. %.



The current century has been distinguished by a continuous rise of CO₂ concentration, which is 418 ppm as of March 2021 according to the Mauna Loa Observatory in Hawaii (USA [12]. This is significantly higher than the pre-industrial, average CO₂ concentration of 277 ppm. If the atmospheric carbon dioxide mass in the real atmosphere doubles, which is supposed to occur in about 120 years, at the current growth rate, the global temperature is expected to increase by 2.0 ± 0.3 K [13].

Carbon dioxide is recognised as a powerful regulator of the Earth's climate. In terms of its greenhouse properties, it occupies the second place after water vapour, and it is the rise of the CO₂

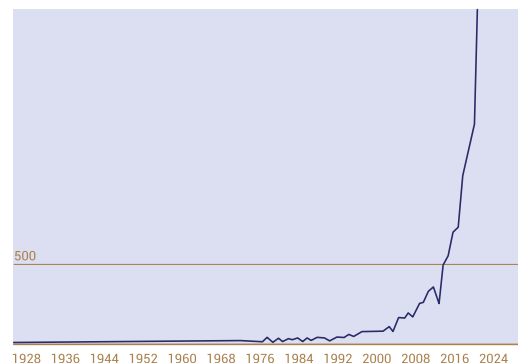
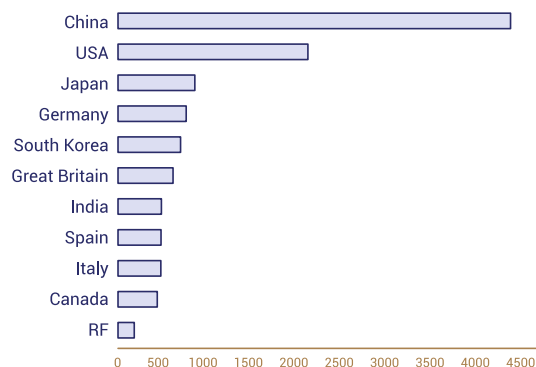
concentration that an increase in the greenhouse effect is associated with. This is determined by the specific features of energy absorption in the infrared spectrum by the CO₂ molecule [14–16].

Interest in scientific development regarding reduction of carbon dioxide emissions by processing them into useful products is constantly growing throughout the world. Over the past 20 years, the Elsevier publishing house has seen an exponential increase (according to the Scopus database) in publications on CO₂ capture and utilisation in international journals, and for 2021, it has provided over 12,000 articles: more than 4,000 publications are from China and 2,000 from the USA; as for Russia - less than 200 so far (fig. 5).

FIGURE 5. Publication activity on CO₂ utilisation in international journals based on the Scopus database.

PUBLICATION ACTIVITY: on CO₂ utilisation

about 12600 documents



Two main technologies are relevant: Carbon Capture and Utilisation (CCU) and Carbon Capture and Storage (CCS), each involving capture and concentration of CO₂ (Fig. 6, 7) at the first stage.

FIGURE 6. The strategy for reduction of anthropogenic CO₂ emissions [17].

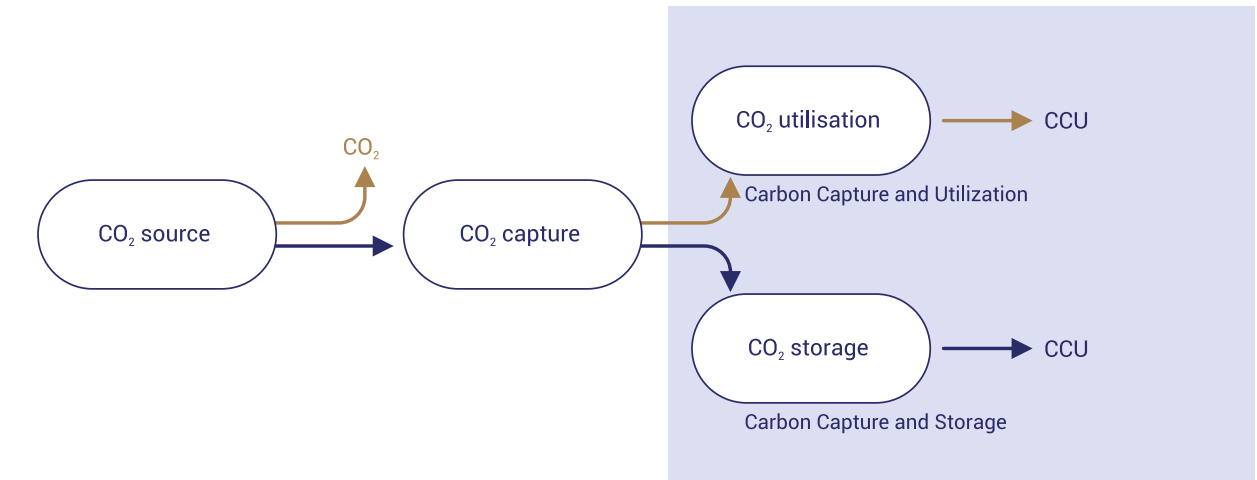
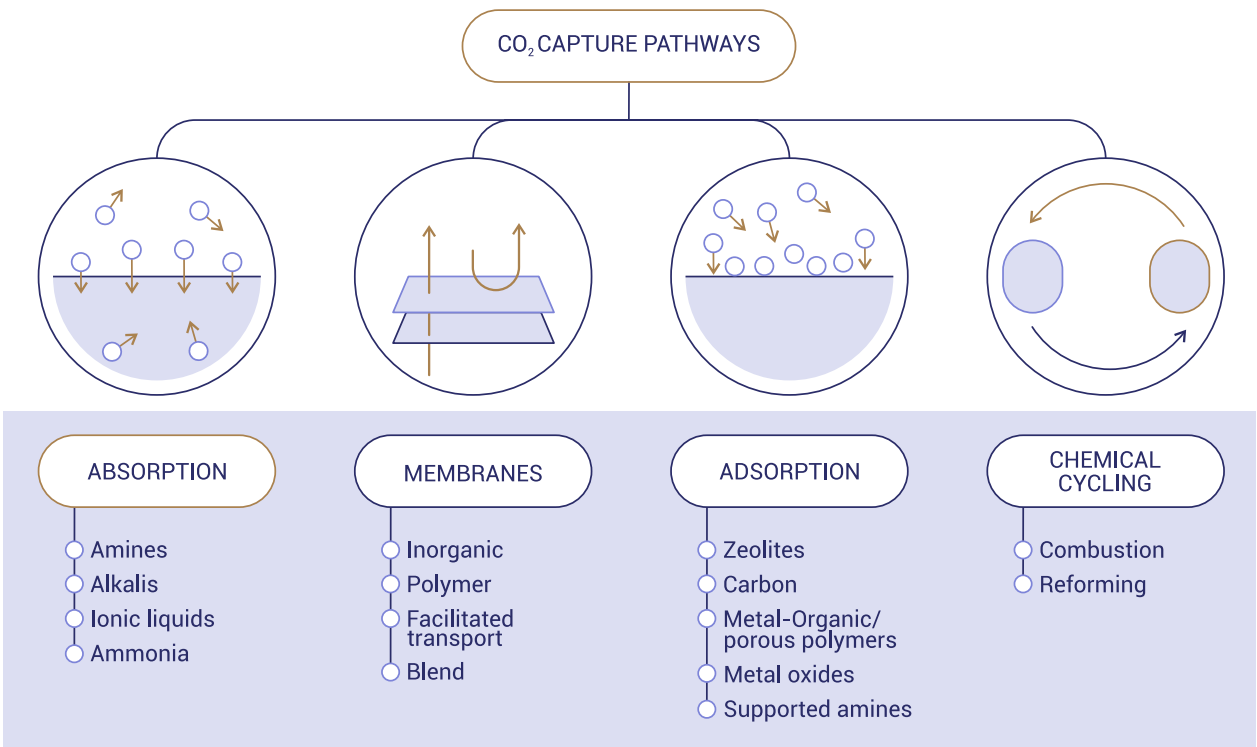


FIGURE 7. Technologies for CO₂ capture [18].



The sorption methods for capturing and concentrating carbon dioxide are very attractive due to their low cost and simplicity of technical solution. Various types of CO₂-adsorbents have been proposed, differing in their chemical composition, texture, morphology and, accordingly, capacity and

selectivity. Sorbents can be conditionally divided into three large groups, depending on the range of their operating temperature: low-, medium-, and high-temperature adsorbents with sorption/desorption temperatures $T < 200^{\circ}\text{C}$, $200^{\circ}\text{C} < T < 400^{\circ}\text{C}$ and $T > 400^{\circ}\text{C}$, respectively [19].

Research of sorption methods for carbon dioxide capturing and concentrating is performed in the following areas:

- Development of methods for obtaining the effective liquid and solid CO₂ sorbents
- Modification of carbon sorbents
- Kinetics of sorption and capacity of carbon sorbents
- Optimisation of conditions for the CO₂ activated carbon sorption

For chemists, utilisation technology (i.e. CO₂ conversion into valuable chemical products and materials) is more attractive. Once captured and concentrated, CO₂ can serve as a precursor for production of many chemical products. At present, the annual volume of CO₂ industrial use is about 120 million tons, which is less than 0.5% of the total annual anthropogenic emissions of CO₂ equal to 34 billion tons. In this regard, expansion of the CO₂ application

as a precursor for chemical processes is a very urgent task aimed at solution of issues of environmental safety and rational use of natural resources.

The general line of the CO₂ chemical utilisation is catalytic conversion into products with a high added value. Currently, large-scale processes for production of urea, salicylic acid, ethylene carbonate, and methanol have been mastered on an industrial scale.

CATALYTIC METHODS OF CONVERTING CARBON DIOXIDE INTO USEFUL PRODUCTS

Converting CO₂ into fuel and valuable products of the chemical industry is one of the most promising ways of CO₂ utilisation. This way of utilising carbon dioxide refers to cyclic technologies when many times are repeated the stages of CO₂ capture, its processing into products and then, emission of CO₂ when using the obtained product. This method does not completely remove CO₂ from the atmosphere but it does reduce the application of fossil fuels. The volume of CO₂ conversion into chemical products (urea, polycarbonates) and fuel (methanol, methane, dimethyl ether, Fischer-Tropsch synthesis products) will reach 0.3–0.6 and 1–4.2 billion tons of CO₂ per year in 2050, which is 4–14 % of the current level of anthropogenic CO₂ emissions - 34 billion tons per year [20]. Advancement of catalytic technologies is expected to raise the energy efficiency, increase the list of processes for obtaining useful products from CO₂ and reduce their cost.

There exists a wide range of technologies for converting CO₂ into useful products with different levels of development – industrial processes, pilot projects and laboratory developments (Fig. 8).

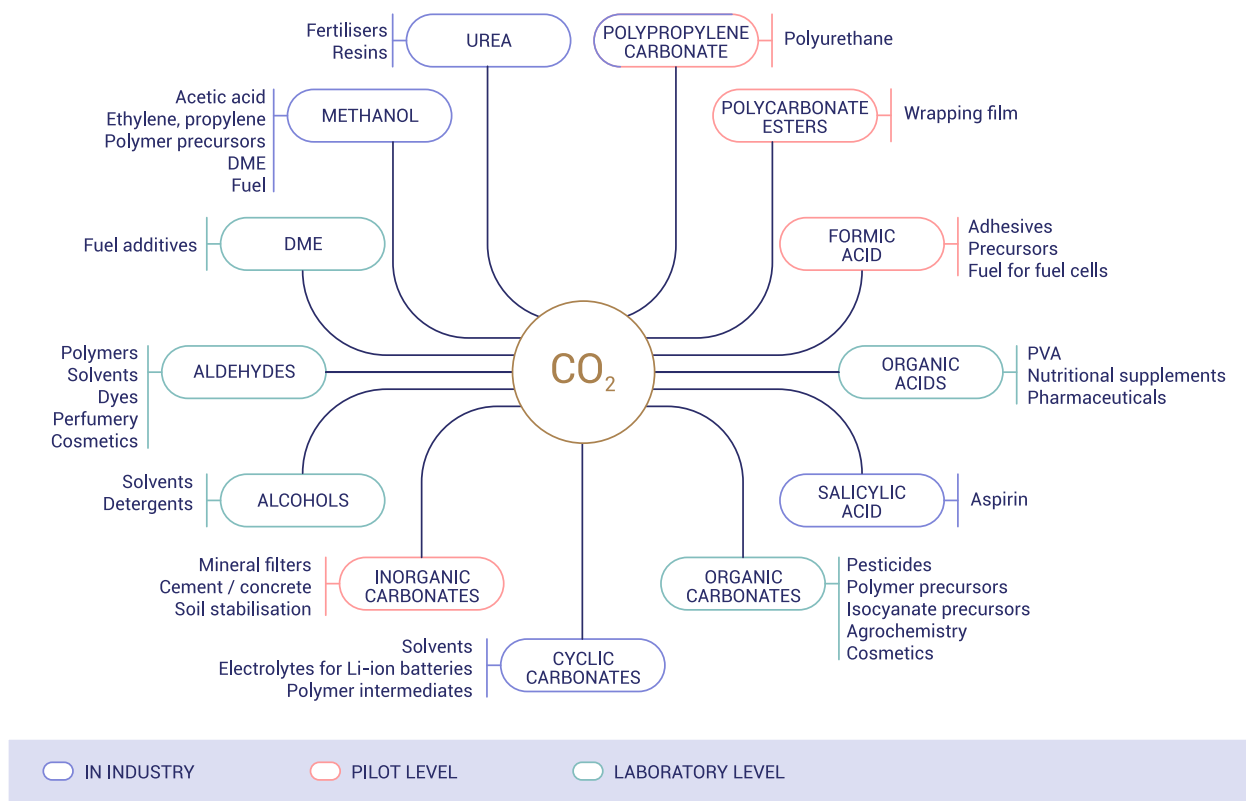
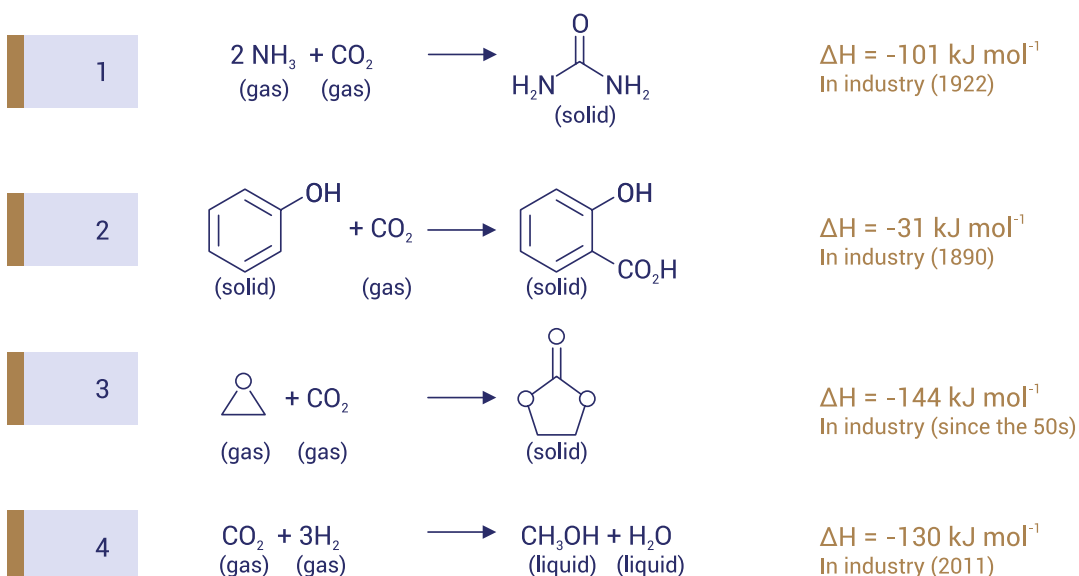
Catalysis is a key technology for an efficient and more sustainable use of resources, which is crucial for the economies of many countries. This provides lower energy processes, reduced waste and pollution,

and improved selectivity in the value-added products for all sectors. Around 90% of all chemical processes use catalysts with the estimated economic impact on 30-40% of the world GDP. Heterogeneous catalysts are already the key component in this sector, ranging from petrochemical plants to catalytic converters for internal combustion engines.

As the world moves toward more sustainable technologies and raw materials to ensure a cleaner future, the role of heterogeneous catalysts is going to gain higher importance. This affords opportunities for a new generation of environmentally friendly catalysts or even demands a glimpse into the past of more traditional catalysts.

Modern industrial world would be impossible without catalysts. Development of chemical products in the developed industrial countries will be technically, economically and environmentally possible only with the help of special catalysts. At present, over 15 international companies manufacture about 100 basic types of solid catalysts. Catalysts play a significant role in industry from an economic point of view and in terms of the environmental pollution reduction.

Nowadays, the chemical products produced from CO₂ on an industrial scale are as follows: urea (1), salicylic acid (2), ethylene carbonate (3), and methanol (4) (Fig. 9).

FIGURE 8. End products of CO₂ processing [21].FIGURE 9. The industrial processes of CO₂ conversion [22].

CARBAMIDE (UREA) PRODUCTION

The capacity of urea plants in the USSR had exceeded 5 million tons per year by the end of 1972 and accounted for more than 30% of the world production. In the 1970s, according to the government's decision, there was purchased urea production equipment with the capacity of 330 and 450 thousand tons per year by technologies of all leading foreign companies.

Ammonia and carbon dioxide convert to urea via ammonium carbamate at the pressure of about 140 bar and the temperature of 180–185°C. Ammonia conversion reaches 41%, carbon dioxide - 60%. The unreacted ammonia and carbon dioxide enter the stripper, with CO₂ acting as a stripper agent. After condensation, CO₂ and NH₃ are

recycled and returned to the synthesis process. The condensation heat is used for steam generation for the CO₂ compressor.

There are over five advanced urea production technologies in the world (Stamicarbon, etc.). Urea 2000plus, one of the new technologies, is successfully used in urea production with the capacity of 2,700 tons/day that was launched in China (CNOOC) in 2004 as well as in production with the capacity of 3,200 tons/day in Qatar (Qafco IV), launched in 2005. At the moment, there are also developments of urea mega-plants with the capacity of up to 5000 tons/day. New energy-saving technologies are used in urea production at the gas chemical plant Gazprom Neftekhim Salavat (Fig. 10).

FIGURE 10. Urea production at the gas chemical plant Gazprom Neftekhim Salavat [23].



A new unit for urea production with the capacity of 600 tons of "Urea-600" per day was put into operation in Veliky Novgorod in 2018. The new production facility was built with the URECON®2006 technology (Fig. 11). Currently, PJSC Acron is modernising its production, which will result in the capacity increase from 600 to 2050

tons/day [25]. The project investments amount to \$85 million. Upon the project completion in 2021, the total annual urea production capacity will increase by 0.5 million tonnes and reach 1.9 million tons, which will make Acron the largest urea production site both in Russia and in Europe.

FIGURE 11. Urea production with the URECON®2006 technology [24].



The use of carbon dioxide in production of this product has very good expansion prospects up to millions of tons because the urea chemical properties determine its widespread use in the chemical industry, in the synthesis of urea-aldehyde (primarily urea-formaldehyde) resins widely used as adhesives, in production of fiberboards and furniture. Urea derivatives are effective herbicides.

Part of the produced urea is used for melamine production. A significant share is used for the Pharmaceutical Industry needs.

By its nature, urea is a mineral fertiliser used for all types of soils for any crops. This form of fertilisation provides a significant increase in the yield of agricultural crops. Compared to the other nitrogen fertilisers, urea contains the largest amount of nitrogen (46.2%), which basically determines the economic feasibility of its use as a fertiliser for many crops on any soil.

In the animal husbandry, urea is added to feed as a protein substitute, and in medical practice, it is used as a dehydration agent.

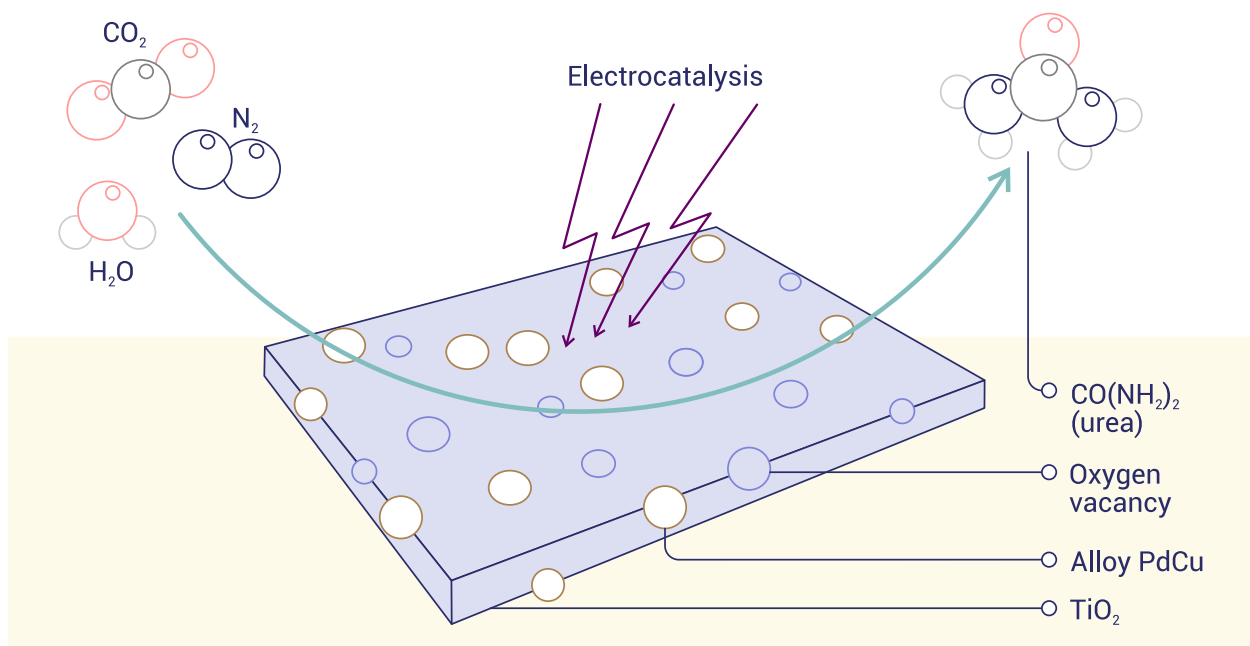
A new large-tonnage area is the use of urea (as a reductant of nitrogen oxides) for cleaning the

emissions from thermal power plants and waste incineration plants.

To achieve compliance of the composition of diesel engine exhaust emissions with Euro-4 and Euro-5 standards, the AdBlue urea solution is used.

In general, at urea production with the volume of ~200 million tons per year, it is possible to utilise up to 150 million tons of CO_2 per year. The process is carried out at the temperature of 185°C and the pressure of 150 bar, CO_2 conversion reaches 85–90%. When assessing the potential of this method of CO_2 utilisation, it is worth taking into account that one ton of urea consumes 0.58 tons of ammonia produced by a very well developed but energy- and carbon-intensive Haber-Bosch process [26]. In this regard, research is underway to develop carbon-neutral technologies for urea production using renewable energy sources. For example, urea has been synthesised from nitrogen, carbon dioxide, and water at room temperature, in the presence of the electrocatalyst made of copper and palladium nanoparticles applied on titanium dioxide (Fig. 12) [27].

FIGURE 12. The scheme of urea electrocatalytic synthesis from nitrogen, carbon dioxide, and water at room temperature [27].

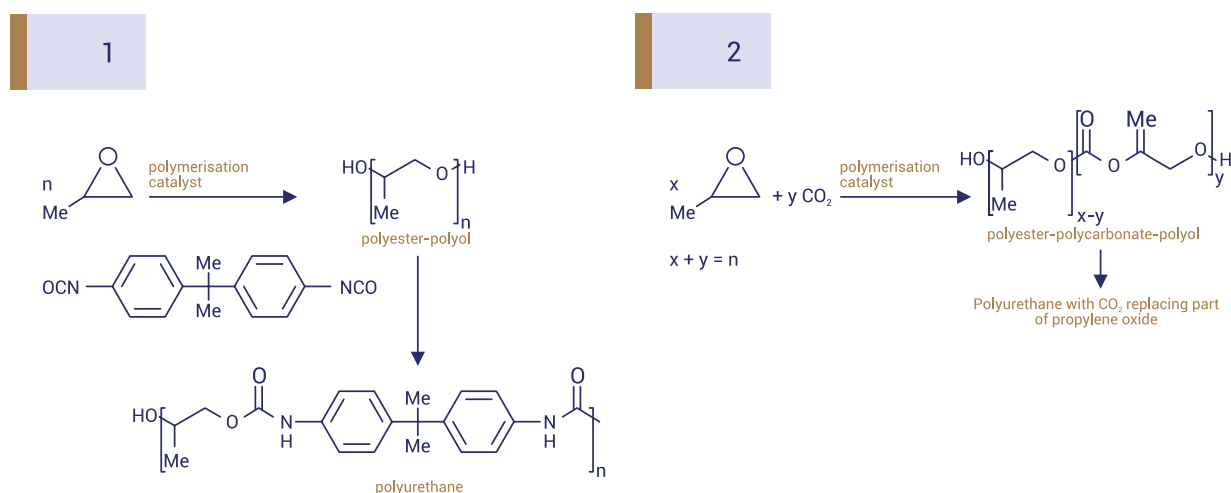


SYNTHESIS OF POLYURETHANES

The next important industrial use of CO_2 is polyurethanes synthesis in which polyols and bis-isocyanates are usually used as precursors [22]. In the traditional Bayer process,

polyol is the simple polyether made from epoxies, such as propylene oxide, the raw material for production of which is fossil fuels (Fig. 13).

FIGURE 13. The scheme of polyurethane synthesis by traditional technology (1) and alternative technology with CO_2 utilisation (2) [22].



In Covestro's alternative DREAM process, polycarbonate polyol (where part of propylene oxide is replaced with carbon dioxide) is used instead of polyol. The capacity of the plant launched in 2016 by Covestro in Dormagen (Germany) is 5,000 tons of polyester carbonate polyol (Fig. 14). Direct

copolymerisation of CO_2 with various epoxides (ethylene oxide, propylene oxide, cyclohexene oxide or isobutylene oxide) is a promising method for synthesis of aliphatic polycarbonates and polycarbonate esters for an important production of biodegradable materials.

FIGURE 14. CO_2 conversion into polymer products at the plant in Dormagen (Germany) [28]. Carbon dioxide instead of crude oil: now the Covestro company includes 20 percent of CO_2 in its polymer component.



The English Company Eonic offers an energy-saving catalytic technology for the CO_2 conversion into polyols [29]. According to [20], the volume of

carbon dioxide conversion into polymer products will have amounted to 10–50 million tons per year by 2050.

SALICYLIC ACID

An important process of using CO_2 as a chemical reagent is the salicylic acid production by the Kolbe-Schmitt reaction; the production volume

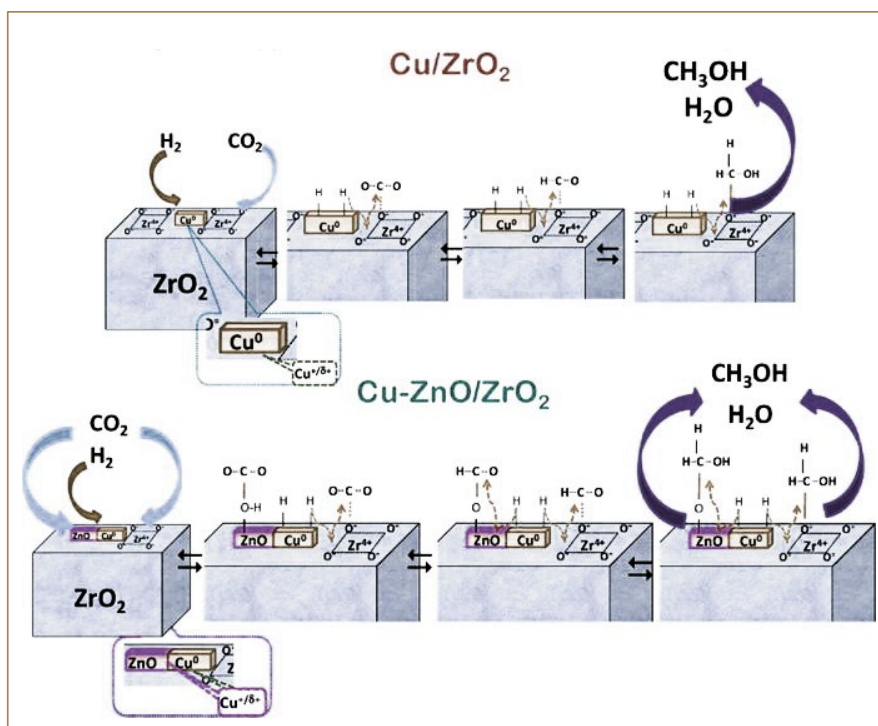
is 0.025 million tons of CO_2 annually, although this is noticeably lower than the volume of its use in the synthesis of urea or polyurethanes.

METHANOL

Methanol is the most important organic substance in the chemical industry, with a global annual production of ~150 million tons [30]. Currently, it is mainly produced by catalytic technologies, from natural gas and coal gasification products. However, some alternative production methods using CO_2 are under development [3, 31, 32] within the framework of a sustainable development concept. To synthesise methanol from carbon dioxide and hydrogen, Cu-Zn-Zr-O catalysts are used that are promoted with additives of various compositions (Ga, La, Ce, Cr, Si, B, Al, In) [3]. It is considered [33] that the reaction involves two active centers: adsorption

and dissociation of hydrogen occur on Cu centers, and adsorption of CO_2 in the form of bicarbonate – on ZrO_2 (Fig. 15). By means of a spillover, atomic hydrogen transfers from the Cu surface to the ZrO_2 surface where the adsorbed carbon and oxygen-containing particles hydrogenate to methanol later desorbed from the surface. Adding of zinc to the catalyst improves copper dispersion and provides additional adsorption centres for CO_2 . Optimisation of the catalyst preparation and reaction conditions resulted in obtaining the following process parameters at 220°C and 2.8 MPa: methanol yield – 12.8%, CO_2 conversion – 20.3%, methanol selectivity – 63.2% [31].

FIGURE 15. Scheme of the reaction for producing methanol from CO_2 in the presence of Cu/ ZrO_2 or Cu-ZnO/ ZrO_2 catalysts [33].



The first modern industrial conversion of CO_2 into methanol has been carried out since 2012 by Carbon Recycling International (CRI) in Iceland (Fig. 16) [3, 34]. The plant's capacity is 4,000 tons of methanol/year. At the same time, the estimated volume of CO_2 involvement in this process is 6,000

t/year. The hydrogen required for this technology is produced by water electrolysis using inexpensive and environmentally friendly energy from hydrothermal sources. CRI has developed an integrated plant project for renewable methanol production with the capacity of 100,000 tons/year (Fig. 17) [36].

FIGURE 16. Conversion of CO₂ into methanol at the plant in Iceland [35].

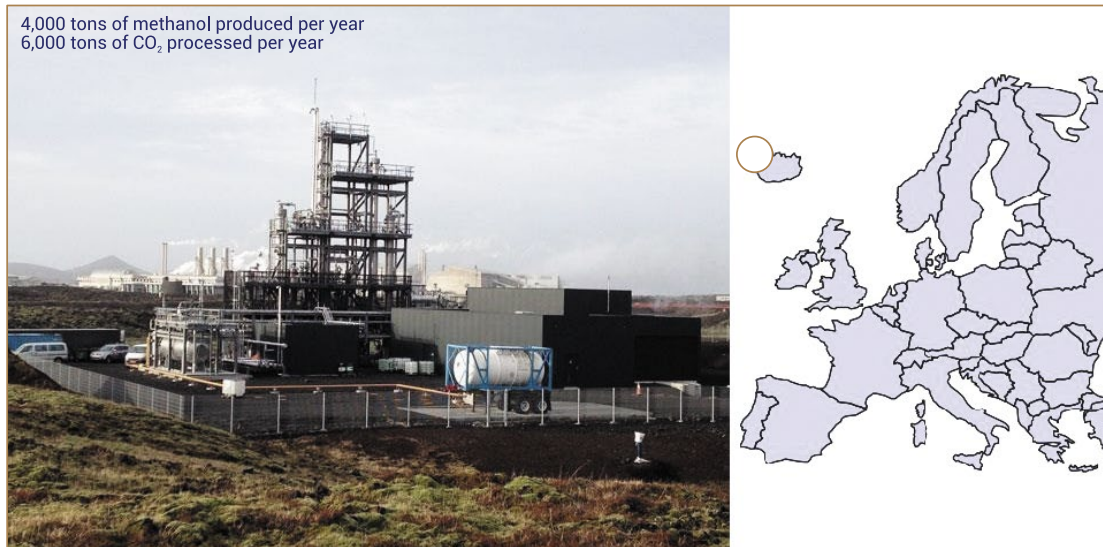


FIGURE 17. 3D visualisation of an integrated plant concept for CO₂ conversion into methanol with the capacity of 100,000 tons of methanol/year [36].



The Canadian Carbon Engineering proposed Air to Fuels, another interesting approach and technology for carbon dioxide conversion using

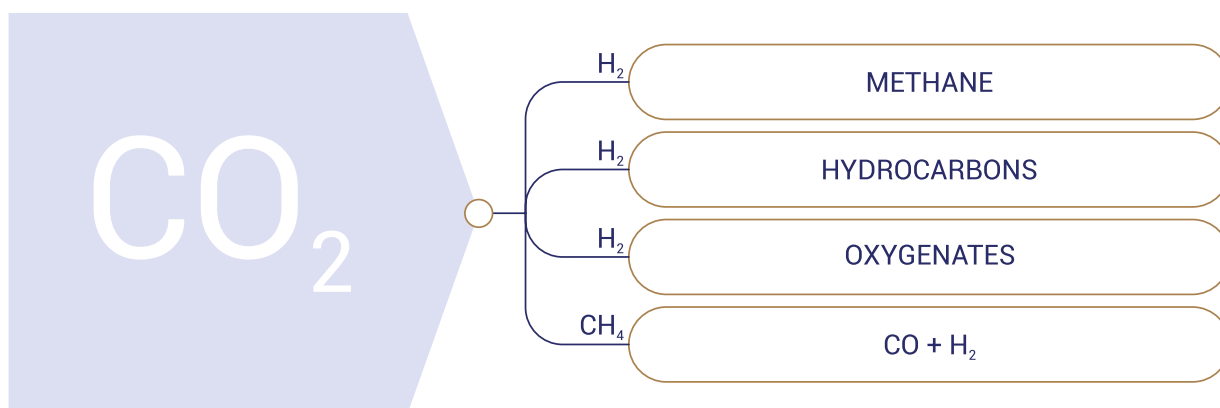
renewable energy sources; it proposes production of carbon-neutral liquid fuel from atmospheric CO₂ and H₂ obtained by electrolysis [37].

CO₂ HYDROGENATION PROCESSES

The next important group of catalytic processes for carbon dioxide conversion are hydrogenation processes with production of methane, higher hydrocarbons, oxygenates or synthesis gas (Fig. 18). Now in the chemical industry, lower hydrocarbons are obtained from

non-renewable natural resources – through dehydrogenation of light alkanes or oil cracking. CO₂ conversion through hydrogenation opens up possibility for production of these valuable compounds from renewable raw materials, which reduces society's dependence on fossil fuels.

FIGURE 18. The main directions of CO₂ conversion by hydrogenation it for production of methane, hydrocarbons, oxygenates, and synthesis gas.



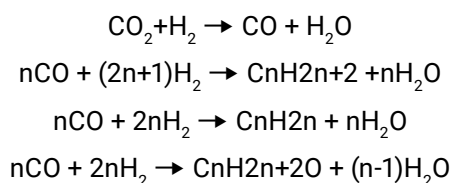
THE CO₂ METHANATION REACTION (SABATIER PROCESS)



Has recently aroused interest as a way of CO₂ use and utilisation in the process of synthesis of substances – energy-efficient carriers for storing and transporting renewable electricity. This process is carried out at the temperature of 250–400°C and an elevated pressure in the presence of catalysts based on Ni, Rh or Ru, providing 100% CO₂ conversion [26]. In 2013, the Audi Company launched a Power-to-Gas (PtG) plant in Werlte (northern Germany) for production of synthetic natural gas from CO₂ and H₂. The plant

includes a 6 MW renewable energy electrolysis unit for hydrogen production and a methanation unit. The scale of carbon dioxide utilisation is still small and amounts to 2800 t CO₂ annually [38].

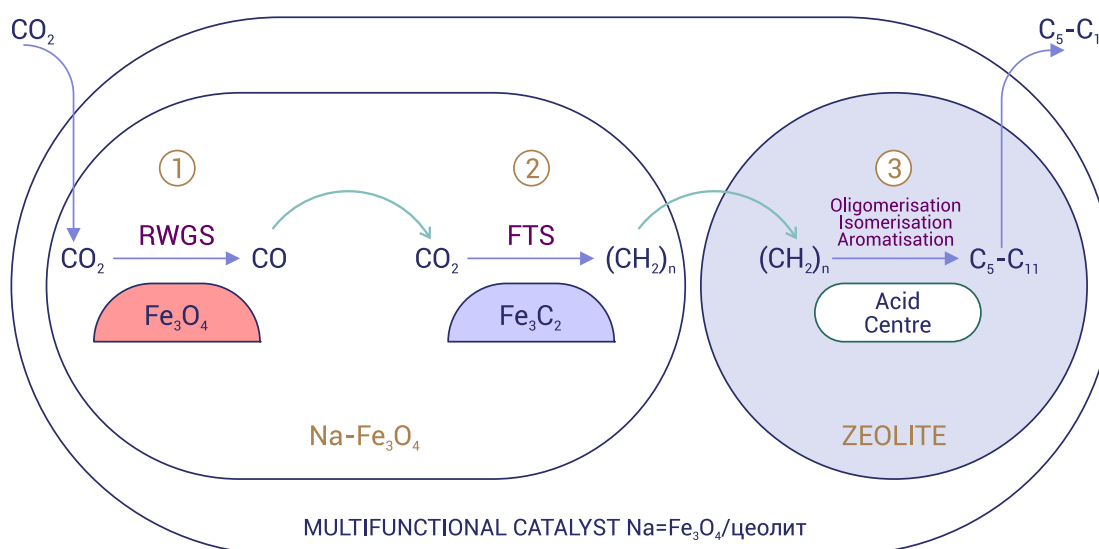
The use of CO₂ in **synthesis of C2-C4 hydrocarbons** – a modified Fischer-Tropsch synthesis process – seems to be a very promising one. This process includes reaction, a reverse reaction of CO conversion with steam and a subsequent hydrogenation of CO with formation of hydrocarbons [26].



Combination of this process with oligomerisation reaction opens up possibility for utilising CO_2 and obtaining hydrocarbons of gasoline fraction containing a mixture of isoparaffins, aromatic and naphthenic hydrocarbons of the $\text{C}_5\text{-C}_{11}$ composition [39]. The uniqueness of this process is that hydrogenation reaction in the presence of multifunctional catalyst $\text{Na} - \text{Fe}_3\text{O}_4/\text{zeolite}$ occurs in three stages (Fig. 19): (1) CO production

by a reverse water gas shift (RWGS) at Fe_3O_4 centres, (2) CO hydrogenation to olefins by the Fischer-Tropsch synthesis (FTS) at Fe_5C_2 centers; and (3) formation of $\text{C}_5\text{-C}_{11}$ hydrocarbons as a result of oligomerisation, isomerisation, and aromatisation of olefins at the zeolite acid centres. Selectivity of hydrocarbon formation is 78% with the CO_2 conversion of 22% [39].

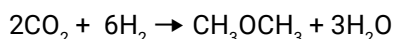
FIGURE 19. The scheme of obtaining $\text{C}_5\text{-C}_{11}$ -hydrocarbons from CO_2 [39].



An important area of CO_2 conversion is synthesis of formic acid $\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$ and dimethyl ether (DME) which are large-tonnage products of the chemical industry and considered as the compounds for storing chemical energy. They serve as hydrogen carrier molecules in the

cycles of storage and transportation of renewable energy [40]. For direct catalytic reduction of CO_2 for obtaining formic acid, both homogeneous systems - organometallic compounds containing Rh, Ru and Ir - and heterogeneous catalysts based on Pt, Pd, Au are used.

DME SYNTHESIS



from CO_2 and H_2 involves sequential hydrogenation and dehydration reactions, which requires the use of bifunctional catalysts containing both metal (for example Cu) and acid

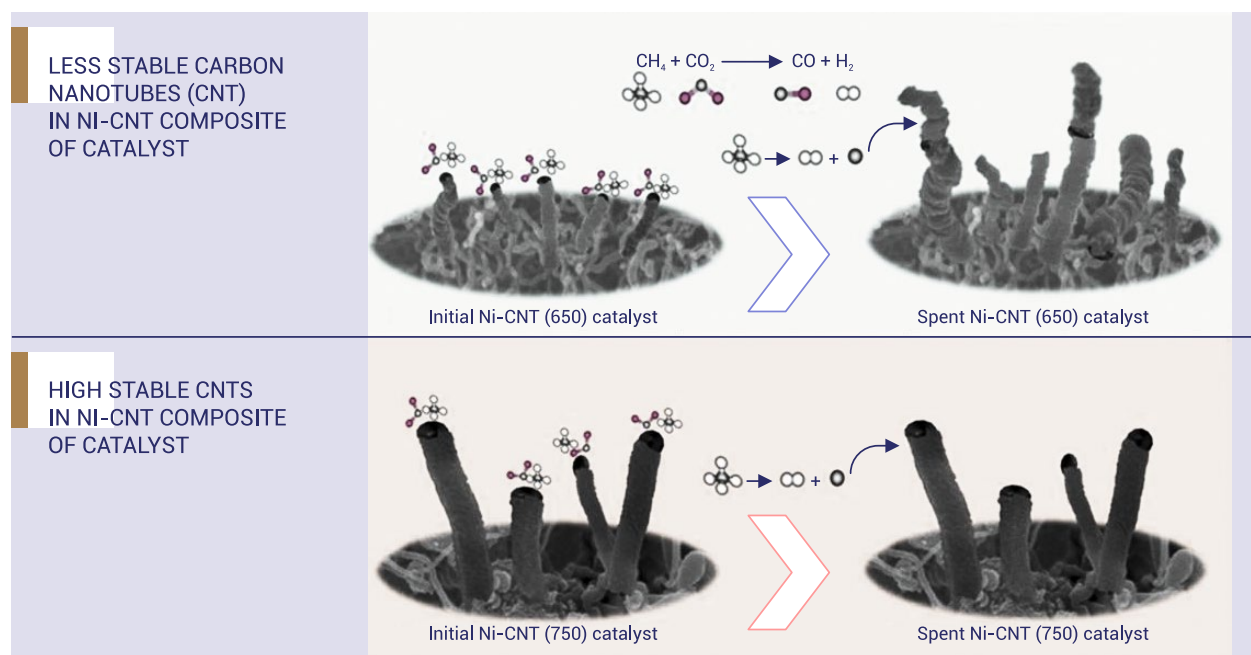
centres. It has been shown that reducing the size of Cu-containing active particles is a successful approach for increasing the efficiency of this process [40].



A special place in catalysis is occupied by **carbon dioxide conversion of methane (CDCM)** which makes it possible to simultaneously utilise two greenhouse gases (CO_2 and CH_4) and obtain synthesis gas as a product, suitable by its stoichiometry (1:1) for further conversion into synthetic fuel according to the Fischer-Tropsch reaction. Nickel catalysts are highly active in this reaction [41]. The process is carried out at the temperature of 800-900°C and under the atmospheric pressure, demonstrating high values

of CO_2 conversion — 80-90%. There is shown the efficiency of composite catalysts where the particles of active component Ni are attached to the top of carbon nanotubes (Fig. 20) [42]. Adding water vapour to the reaction mixture expands the stability area of the system to formation of carbonaceous deposits, allows optimisation of the process parameters, providing the given completeness of conversion of reagents and the required composition of the resulting synthesis gas [43].

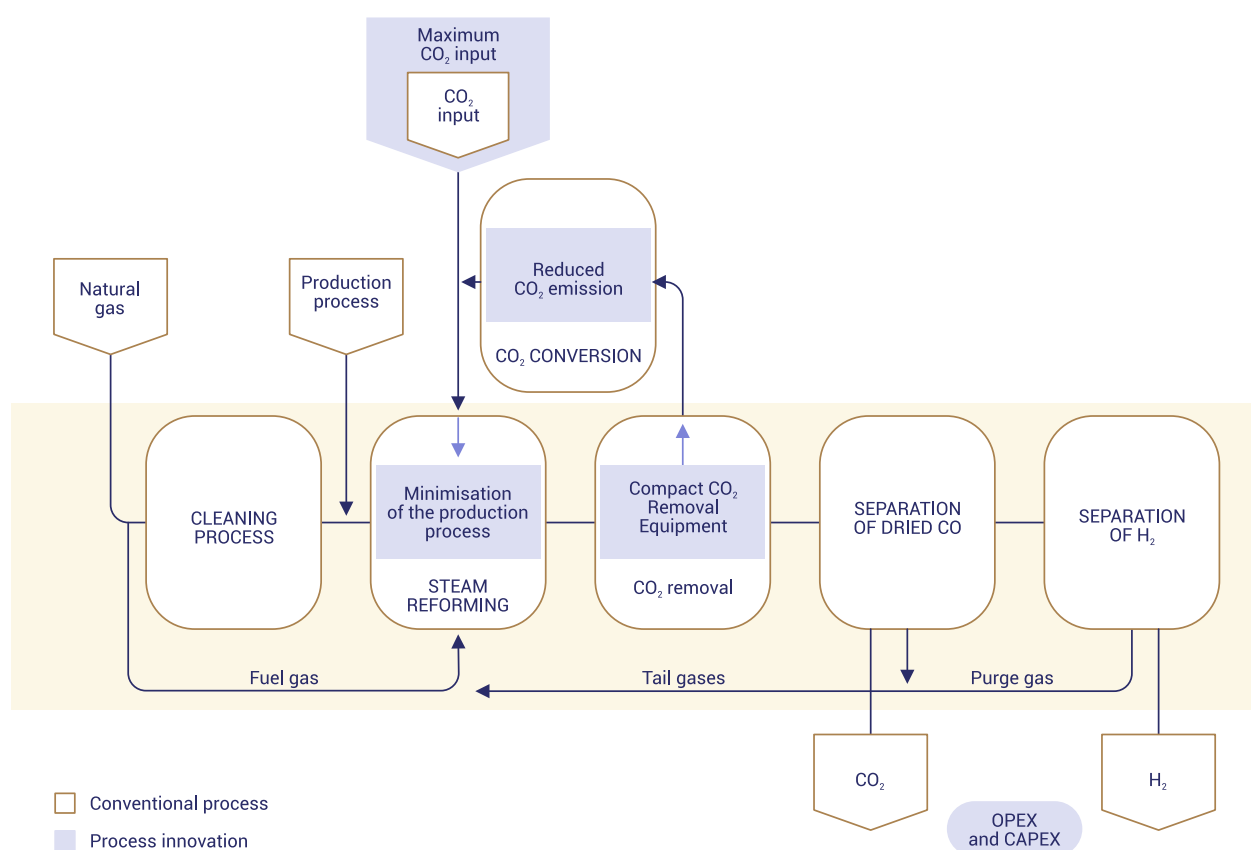
FIGURE 20. Composite Ni catalysts for carbon dioxide reforming of methane [42].



The Linde Company has developed DRYREF™ SMR technology in collaboration with BASF for improvement of the energy and economic efficiency of steam reforming and carbon dioxide utilisation [44]. According to the proposed scheme (Fig. 21), CO_2 is added to the reaction mixture

containing natural gas and water. As a result, carbon footprint of the synthesis gas production reduces, steam consumption decreases, and synthesis gas is obtained with a lower H_2/CO molar ratio as compared to the parameters for steam methane reforming.

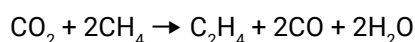
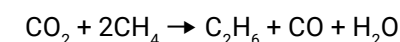
FIGURE 21. Flow diagram of the DRYREF™ SMR process [44].



PROCESSES WITH CO₂ AS A MILD OXIDANT

Processes in which CO₂ acts as a mild oxidant [45–48] are studied at the laboratory

level. In the oxidative condensation of methane (CO₂-OCM)

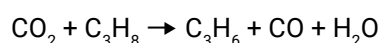
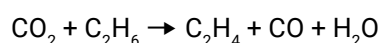


with formation of ethane and ethylene in the presence of a catalyst (MnO-SrCO₃, ZnO-CeO₂ or

CaO-CeO₂), the CO₂ conversion is 5–7%, the yield of C₂ hydrocarbons is up to 5–7% [48].

Reaction of oxidative dehydrogenation of light alkanes with CO₂ participation is carried out at 650–700 °C in the presence of various catalysts (Pd/CeZrAlO_x, CoMo/CeO₂, GaN/SiO₂) [47]. The yield of target products

(ethylene, propylene) reaches 70%. The use of photocatalytic systems makes it possible to use a renewable energy source and to carry out the process under mild conditions (Fig. 22).



A promising process will be the use of CO₂ for **oxidative dehydrogenation of alkyl aromatic**

hydrocarbons with obtaining styrene and its homologues [39].

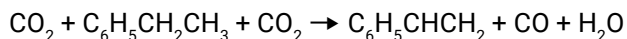
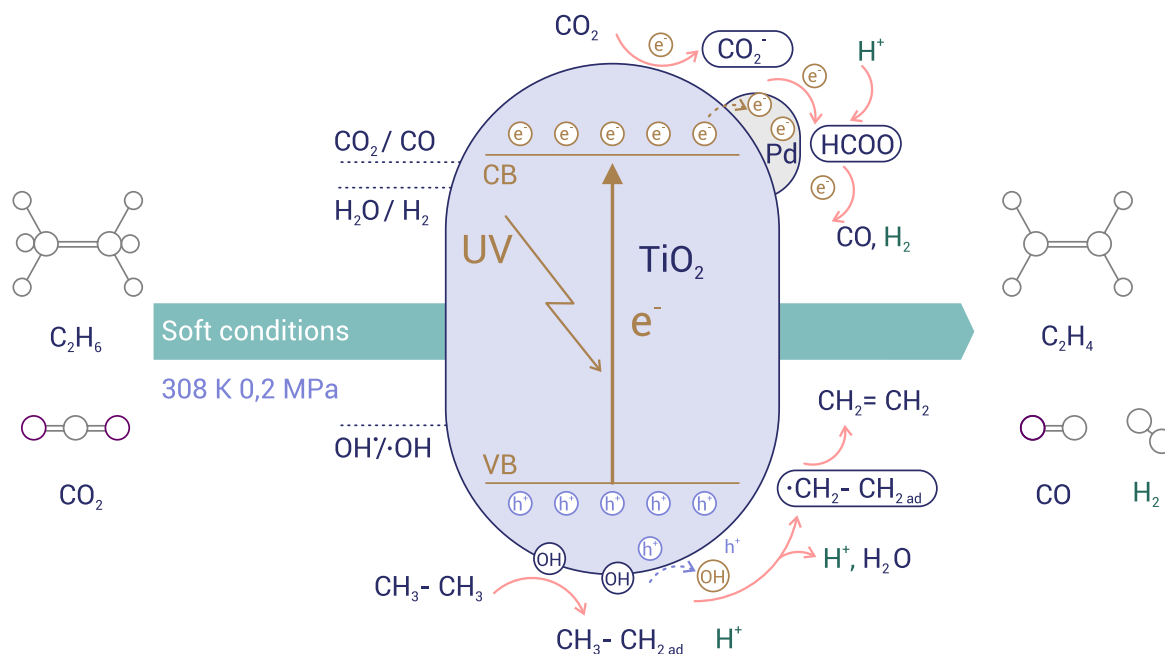


FIGURE 22. The mechanism of photocatalytic oxidative dehydrogenation of ethane with the use of CO₂ as an oxidant in the presence of a Pd/TiO₂ catalyst [48].



CONCLUSION

Chemical reactions and heterogeneous catalysts used to convert CO₂ to such valuable chemicals as urea, methanol, polyurethanes, CO, CH₄, C₂H₄ were under discussion in this review. The CO₂ molecule is very stable in terms of thermodynamic properties; its activation requires a lot of energy, and production of this energy itself sometimes goes with release of CO₂. For that reason, to achieve the total effect of reducing CO₂ emissions, it is necessary to develop new efficient catalysts for conversion of CO₂. The catalytic conversion of CO₂ can take place in a gas phase, in a liquid phase or in electrochemical cells. Since solubility of CO₂ is rather low in an aqueous solution, conversion of CO₂ in the liquid phase

usually suffers from low productivity. In this brief review, we have mainly considered the processes in the gas phase with participation of catalysts: metal oxides, supported metals, carbides, carbon materials.

Homogeneous catalysts in the formic acid production are still lagging behind in application due to a low solubility of CO₂; development of an active heterogeneous catalyst for this process has very good prospects.

The processes using heat and light as energy sources will undoubtedly be required to minimise overall energy consumption. Electrochemical conversion of CO₂ using catalysts is still at an early stage and requires further optimisation.

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