

# Sequestration of Carbon Dioxide by Recycling Technology

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## Abstract

Increase of carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere due to human industrial activity makes significant contribution to global warming: 38 Bln. tons of CO<sub>2</sub> are released to atmosphere per annum, while over 80% of that amount is due to burning fossil fuel. That is why research and development of CO<sub>2</sub> release reduction technologies – sequestration – is a prominent and urgent need.

CO<sub>2</sub> sequestration in general includes the following processes:

- CO<sub>2</sub> build-up in the biomass of crops and plants, aquaculture and soil humus.
- CO<sub>2</sub> underground storage and burying in the gas/oil, coal and rock salt reservoirs, or capture in the waste rock materials.
- CO<sub>2</sub> recycling to produce valuable chemical products.

Advantages of CO<sub>2</sub> recycling technologies are not only the reduction of CO<sub>2</sub> releases to atmosphere, but also production of valuable chemical products. There are considered three ways of CO<sub>2</sub> recycling:

- Catalytic CO<sub>2</sub> recycling process, based on use of efficient catalysts, which reduces energy consumed for CO<sub>2</sub> conversion while ensures high process selectivity and high product output.
- Plasma-chemical CO<sub>2</sub> recycling process is based on chemical reactions which proceed in a cold and non-equilibrium plasma of microwave discharge.
- Radiation-chemical CO<sub>2</sub> recycling process is based on chemical reactions induced by ionizing irradiation.

It is shown that industrial technology of CO<sub>2</sub> recycling achieves self-recoupment within 4 to 5 years through the use of appropriate combination of catalytic, plasma-chemical and radiation-chemical processes of CO<sub>2</sub> recycling.

## Introduction

Increase of carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere due to human industrial activity makes significant contribution to global warming: 38 Bln. tons of CO<sub>2</sub> are released in atmosphere per annum, while over 80% of that amount is due to burning fossil fuel. In case no actions will be undertaken global atmospheric release of CO<sub>2</sub> may increase 3 times by year 2100 in compare with the 2020 one followed further increase of temperature of the atmosphere and the oceans and inevitable climate change. That is why research and development of CO<sub>2</sub> release reduction technologies – sequestration – is a prominent and urgent need [1].

During 2021 shares of CO<sub>2</sub> releases in the global scale have been distributed in a following order [2]: China - 32,9%, USA - 12,9%, EU - 7,3%, India - 7,0%, Russia - 5,1%, Japan - 2,9%. During 2022 [3] CO<sub>2</sub> releases due to global power production have increased on 320Mt.

By year 2050 European Union is intended completely to ban the energy generation followed CO<sub>2</sub> releases to atmosphere. To accomplish that goal EU has introduced the «carbon

tax» (about 100 Euro per ton of CO<sub>2</sub>). The tax should be paid by industrial companies in accord to their CO<sub>2</sub> releases.

### Brief Overview of Carbon Dioxide Sequestration and Recycling Technologies

Carbon Capture and Storage (CCS) - is a process of CO<sub>2</sub> capture, transportation and storage/ burying or final disposal. In a general sense CO<sub>2</sub> sequestration includes the following processes:

- a) CO<sub>2</sub> build-up in biomass of plants, crops, aquaculture and soil humus.
- b) CO<sub>2</sub> capture and underground storage and burying in the gas/oil, coal and rock salt reservoirs, or final disposal in the spent rock materials.
- c) CO<sub>2</sub> recycling to produce valuable chemical products.

CO<sub>2</sub> sequestration technologies are nowadays developed by many commercial companies and organizations all over the world, while the technologies are already in use in the countries such as Australia, Great Britain, Island, Netherlands, Norway, Russia, USA etc.

The advantages of CO<sub>2</sub> sequestration in a biomass are relative technological simplicity, input in recovery of green spaces and soils remediation. The drawback - large space area which should be allocated for this purpose, delayed effect in terms of CO<sub>2</sub> sequestration when planting perennials, dependence of CO<sub>2</sub> uptake on season and sun activity, and potential negative impact on the environment while using monocultures or gen-modified plants and aquacultures. Thus, in the middle latitudes of Northern hemisphere the maximum uptake of CO<sub>2</sub> by plants and crops occurs in May and June, while a limited amount of CO<sub>2</sub> is uptaken just coniferous trees during winter time.

The advantages of CO<sub>2</sub> sequestration in underground reservoirs are maturity of technology, availability of existing disposal sites, availability of required gas-transportation and gas-pumping infrastructure, relative simplicity of implementation. The drawbacks are lack of data on safe terms of facility operations, potential simultaneous ingress of large quantities of CO<sub>2</sub> to the environment in case of technogenous accidents or natural disaster and operational expenditures to maintain the facility in a working condition.

The advantages of CO<sub>2</sub> recycling technologies are that in addition to reducing CO<sub>2</sub> releases to atmosphere one can produce valuable chemical products. The drawback is that in a general case the technology readiness level still requires additional investments in technology refinement, aprobatation, piloting and scalability.

Obviously, the use of any of CO<sub>2</sub> sequestration technologies will increase CAPEX and OPEX of a product manufacturing due to increased power consumption by 20 to 100%. However imposing a «carbon tax» and it consequent further increase will also result in increase of the product cost in a similar or even higher manner for all enterprises with a high «carbon footprint». For that reason one can see a boom of private and governmental investments in R&D of

CO<sub>2</sub> sequestration and recycling technologies to do not be late in the race for the «carbon footprint» reduction.

Thus, Climeworks company captures CO<sub>2</sub> of ambient air since 2022 and pumping it into underground reservoirs with further conversion in a solid rocks. Several companies have made advance payments to Climeworks for future service of CO<sub>2</sub> sequestration. Climeworks has also received over 780M USD on technology further development from wide range of independent investors.

In 2023 U.S. Department of Energy has granted 1.2 Bln. USD to Carbon Engineering Company on creation of additional capacity for CO<sub>2</sub> storage. Two projects of CO<sub>2</sub> capture and storage should be developed in Texas and Louisiana in frame of the grant. CO<sub>2</sub> should be disposed in underground reservoirs or converted in a useful products.

Mitsubishi Shipbuilding Co. in 2023 has built the first in the world cargo ship to transport liquified CO<sub>2</sub> (LCO<sub>2</sub>) [4]. It is also developing tankers to transport both ammonia and liquified CO<sub>2</sub>. The tankers can transport ammonia (as a future fuel) to power plants on direct way and return back CO<sub>2</sub> for disposal or recycling.

State Atomic Energy Corporation «Rosatom» is also working on reduction of a «carbon footprint», including implementation assessment of technological solutions in production of CNG, low-carbon hydrogen and ammonia as well as in energy production and storage.

PSC «Norilsky Nikel» is implementing R&D for reduction of the «carbon footprint» and transfer to low-carbon paradigm using CO<sub>2</sub> for artificial mineralization of waste rock at the company tailings dump with formation calcites and other minerals.

PSC «Novatek» [5] is going to reduce release of greenhouse gases at oil production on 6% by 2030: from current 12,58 tons of CO<sub>2</sub> per thousand barrels of oil equivalent. They have developed the concept of CO<sub>2</sub> capture and storage in underground reservoirs. Each of 2 geological reservoirs at the licensed site have potential capacity of 600 Mln. tons of CO<sub>2</sub> [6].

Recycling of CO<sub>2</sub> can be done by reduction with hydrogen and producing various products including soot, methane and other hydrocarbons, methanol, formic acid, urea etc. These processes allow produce valuable chemical products (or precursors) from CO<sub>2</sub> and the products can be used during further production of complex products in industry, agriculture and on transport.

CO<sub>2</sub> can also be recycled with plasma-chemical and radiation-chemical processes converting carbon dioxide into various organic compounds, or solids; this allows substantially reduce power consumption for the process implementation in compare to purely chemical or electro-chemical technologies.

Number of products, which can be produced from CO<sub>2</sub> is quite extensive. In case the recycling technology would be economically justified, CO<sub>2</sub> should be a highly demanded raw material for production of many chemicals such as dimethyl ether, carbon monoxide, ethylene, methanol, formic acid etc.

## Discussion

Catalytic method of CO<sub>2</sub> recycling is known quite well and is based on high efficient catalysts reducing energy needed for conversion of very stable CO<sub>2</sub> molecule, providing high selectivity and output of the target product.

Plasma-chemical method of CO<sub>2</sub> recycling is based on chemical reactions occurring in the cold non-equilibrium plasma of microwave discharge. CO<sub>2</sub> decomposition proceeds at ambient temperature and atmospheric pressure, that is highly beneficial in compare to CO<sub>2</sub> thermal dissociation, which take place at the temperature over 1270K. By changing the gas mixture composition one can manage the composition of a target products.

The radiation chemical method of CO<sub>2</sub> recycling is based on chemical reactions induced by ionizing radiation - radiolysis. Radiolysis rate does not depend on the temperature, but governed irradiation dose rate. In addition it was found that carbon oxides radiolysis rate in particular conditions is strongly increasing due to a chain reactions [7]. Irradiation facilities are currently used elsewhere to clean-up exhaust gases of coal powered plants with production of nitrogen fertilizers.

For industrial technology of CO<sub>2</sub> recycling the best efficiency can be achieved by combining catalytic, plasma-chemical and radiation-chemical processes and synthesis of valuable chemical products. The recycling technology is quite timely on market due to implementation of the global «green» agenda [8].

As a solution of the problem of «carbon footprint» reduction the authors propose to implement environmentally safe and efficient industrial technology:

1. CO<sub>2</sub> removal from effluent gases of fossile power plants/ enterprises;
2. CO<sub>2</sub> conversion into condensed state for transportation to recycling site;
3. CO<sub>2</sub> interim storage in permafrost;
4. CO<sub>2</sub> recycling in demanded chemical products (carbon monooxide, syngas, soot, oxygen, hydrocarbons, methanol, urea etc.);

CO<sub>2</sub> exosted by fossile power plants and enterprises is used as a raw material after pretreatment. Follow the pretreatment CO<sub>2</sub> is liquified or freezed into solid sate onsite. Solid CO<sub>2</sub> is quite stable at ambient temperature and pressure. Liquified/solidified CO<sub>2</sub> is transported for recycling or interim storage: liquified CO<sub>2</sub> - by railroad or cargo ships in pressurized tanks, while solidified CO<sub>2</sub> (dry ice) - in 20/40 feet shipping containers.

CO<sub>2</sub> interim storage can be arranged in a galleries or wells in a permafrost taking into account depth of the permafrost layer. The advantages of such way of interim storage is: permafrost occupies over 50% of the Russian territory and some other northern countries. At low temperatures power consumption for CO<sub>2</sub> storage is reduced, while freezed CO<sub>2</sub> prevents surrounding permafrost of

degradation and simultaneously reduce release of other «green» gases e.g. methane to atmosphere.

Options of CO<sub>2</sub> sequestration by recycling:

Option 1. Deployment of CO<sub>2</sub> recycling capacities onsite, i.e. nearby fossile power pant/enterprise and it recycling either in precursors or target products.

Option 2. Deployment of CO<sub>2</sub> recycling capacities nearby to sea ports.

Option 3. Receiving CO<sub>2</sub> from customers in a condensed state and it further transportation to interem storage or recycling facility.

Some figures to prove the recycling technology commercial viability: e.g. for 165MWt fossile power plant and target level of CO<sub>2</sub> release reduction - 5% by year 2030 it is required to deploy 4,5MWt recycling facility (either linear accelerator or gyrotron). Taking into account CAPEX and OPEX a simple payback period of the deployment will be 4 to 5 years due to production of commercial products CO<sub>2</sub> and «carbon tax» (e.g. in EU - CBAM).

As a commercially valuable products one can suggest the following:

1. Carbon monoxide - CO or mixture of carbon monoxide and hydrogen - synthesis gas(syngas). Syngas is used to produce hydrocarbons by the Fishcer-Tropsch method. The Fischer-Tropsch method [9] to produce target products from syngas, including methanol, is very capital intensive, in particular, syngas production takes up to 60% of overall expenditures. That is why industrial implementation of CO<sub>2</sub> recycling technology and carbon monoxide (or syngas) production for the end-users will be highly demanded.

2. Urea (NH<sub>2</sub>)<sub>2</sub>CO, or carbamide is a very demanded fertilizer. To produce 1 metric ton of carbamide it's required 0,73 ton of CO<sub>2</sub>, 0,57 ton of NH<sub>3</sub> and 3,3 GJ of steam.

For 165MW fossile power plant annual release of CO<sub>2</sub> is 570 000 tons. To achieve carbon neutrality 1565 tons of CO<sub>2</sub> should be recycled daily. This corresponds to production of 2135 tons of carbamide per day. Power consumption for the production will be about 8% of the power plant capacity.

Commercial success of CO<sub>2</sub> sequestration/recycling technology implementation will depend on the measures of governmental support. Thus, in EU decarbonisation is supported with governmental funding in the form of subsidies, grants, preferential loans which are provided for the decarbonization projects. Long term subsidies for CO<sub>2</sub> recycling equipment manufacturing and installation will ensure CO<sub>2</sub> increased self-sufficiency, while equipment manufacturers will get opportunity and more important - stimulus to reduce substantially CO<sub>2</sub> atmospheric releases.

Carbon monoxide world market volume in 2022 reached 3,26 Bln. USD and accordingly to forecasts [10] by 2030 will increase up to 4,53 Bln. USD. Carbon monoxide is used in farma and biotech industry, ore mining and processing, chemical industry, metalworking and electronic industry. The factors which support

the growth of carbon monoxide market are increased demand on the mass chemical products as well as increased demand on goods in fish and meat packaging sector.

Implementation of the proposed recycling technology of CO<sub>2</sub> sequestration will increase demand on «green» energy production such as: Nuclear, Wind, Solar or Hydro Power Plants. The technology will utilize excess of energy, generated by wind and solar power plants in peak periods.

From the research results it is seen that CO<sub>2</sub> sequestration and reduction of «carbon footprint» can be done as an appropriate combination of radiation-chemical, plasma-chemical and catalytic ways of CO<sub>2</sub> recycling with synthesis of valuable products. Development and scaling of CO<sub>2</sub> recycling technologies will allow:

- a) Avoid «carbon tax» burden for enterprises with a high «carbon footprint».
- b) Create high-tech industrial production.
- c) Benefit of good competitive edge in frame of ESG agenda.

## Conclusion

The authors are proposing to implement industrial recycling technology of CO<sub>2</sub> sequestration by combining catalytic, plasma-chemical and radiation-chemical processes to convert CO<sub>2</sub> into carbon monoxide 6 syngas, other substances or solids. The technology allows significantly reduce power consumption for CO<sub>2</sub> recycling in compare to just chemical or electro-chemical technologies.

Success of industrial deployment of CO<sub>2</sub> recycling technologies will depend to some extent on the measures of governmental support. The best commercial potential has the technology which combines radiation, plasma and catalytic methods of CO<sub>2</sub> recycling followed synthesis of valuable chemical products Industrial

implementation of the proposed CO<sub>2</sub> recycling technology will increase demand on energy produced by «green» and renewable sources such as: nuclear, wind, solar and hydro power plants.

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## Conflict of Interest

The authors declare no conflict of interest.

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