Review of technologies for capturing carbon dioxide from industrial emissions as part of reducing the carbon footprint of plants and useful applications in water-gas stimulation techniques for enhanced oil recovery

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Abstract. The article discusses the importance of finding effective technological solutions for CO₂ capture and subsequent utilisation in the context of underground storage or underground injection of carbon dioxide in order to implement water-gas effects to enhance hydrocarbon recovery. The authors also focus on current and promising carbon capture methods, comparing their technological features, advantages and disadvantages. Conclusions are drawn about which technological developments may be the most promising for solving the problem of reducing the carbon footprint of energy industry enterprises, and where there is a need for further research, despite the high energy costs and technological complexities.

1 Introduction

Changing our approach to energy production is critical to reducing our environmental footprint. The complexity of tackling climate change requires a constant search for new solutions. One of the most important ways to reduce emissions is to replace outdated fossil-fuelled power plants with newer ones that utilise renewable energy sources. Focusing on improving the efficiency of industrial and energy plants that are a source of greenhouse gas emissions is also an effective method [1]. More research and investment in the development and implementation of innovative technologies aimed at reducing the negative impact on the climate is also an important aspect.

Despite the great success in the development of the basic technology of carbon dioxide capture and underground storage (CCS), some of the most promising solutions have recently become increasingly recognised as CCUS and CCU [2]. One of the key aspects of such technologies is not only the ability to capture large amounts of carbon dioxide, but...
also the efficiency of its subsequent physicochemical conversion, which makes it possible to use CO$_2$ as a valuable feedstock for creating a variety of useful energy carriers such as methanol, various fuels, materials for construction, and other chemical compounds [3]. In addition, carbon dioxide can be utilised as a method to increase the efficiency of hydrocarbon production from oil and gas reservoirs through a process known as CO$_2$-EOR, which involves injecting carbon dioxide as an agent into oil and gas reservoirs [4]. This opens up new prospects for the use of carbon dioxide not only as a waste, but also as a raw material for the production of useful products.

Despite the progress in recent decades in the development and deployment of renewable energy technologies, they remain capital intensive in most cases, which reduces their competitiveness compared to fossil fuels in some projected scenarios of the world energy system [1]. As fossil fuels are likely to continue to play a major role in the future energy mix of the world, alternative scenarios need to be considered where their continued use is consistent with clean technology solutions within the current decarbonisation agenda.

The oil and gas industry sees quite promising technologies related to the mechanisms of carbon dioxide capture and sequestration from industrial sources and further injection as an active agent (mainly as part of a water-gas mixture) into the developed oil and gas underground horizons to increase hydrocarbon recovery within the framework of enhanced oil and gas recovery (EOR) methods [5]. Further we will consider and compare various traditional and prospectively developing technologies of carbon dioxide capture for further use as a potential raw material in the intensification of hydrocarbon production at oil and gas fields.

2 CCS, CCU or CCUS?

As discussed earlier, the traditional concept of reducing greenhouse emissions through carbon capture and underground storage (CCS), which can still provide huge opportunities for direct emission reductions, is no longer so rational today. CCS is being intensively transformed into CCU and CCUS technologies, which include both the direct utilisation of CO$_2$ and its conversion by physicochemical or biological processes into new useful products. The CCU technology, the application of which, at first glance, is much less efficient from the calculations of the volumes of direct utilisation of carbon dioxide and the arising probability of associated CO$_2$ emissions in the process of obtaining useful energy carriers and the end of the product life cycle, nevertheless has its advantages [6].

For example, this type of chemical carbon dioxide utilisation (CCU) typically does not require transportation, as CO$_2$ processing plants can operate directly on the premises of the plant or facility whose emissions are to be utilised. The beneficial use of captured carbon dioxide to produce valuable chemical products can reduce the cost of source capture processes by generating additional revenue from the sale of end products or reducing costs by using the resulting raw materials directly at industrial facilities.

Despite the actively developing CCS and CCU projects, CO$_2$ enhanced oil recovery (CO$_2$-EOR) technology already has significant experience in oil and gas applications and is ready for widespread commercial deployment, compared to other CO$_2$ sequestration methods. Analysts [7] estimate that more than 260 million tonnes of CO$_2$ have already been injected and stored through enhanced oil recovery (EOR) operations and technologies. Although this EOR method is not suitable for every oil field, this method of stimulating the flow of hydrocarbons and increasing their production is a widely tested and common operation in the oil and gas industry.

In the context of the Russian oil and gas production industry, interest in carbon capture, utilisation and storage (CCUS) projects increases significantly when considering the prospect of using CO$_2$ to improve hydrocarbon production efficiency and increase oil
recovery. Such initiatives are particularly attractive due to the possibility of utilising additional oil revenue to fund these projects [8].

The possibility of creating industrial projects for carbon dioxide capture and storage in Russia has not yet been realised. However, the country's oil and gas industry continues to develop, which creates a favourable base for the rapid emergence of such projects. Studies conducted by the IEA and MIT show that Russia has impressive CO₂ storage capacity that exceeds analogues in other countries [7, 9]. Due to the already developed infrastructure in the exploited fields, the implementation of measures to reduce carbon dioxide emissions and carbon footprint will not require significant investments. "VYGON Consulting" [8], based on official data on mineral reserves in Russia, indicates that the country's oil and gas fields alone can hold up to 305 gigatonnes of CO₂.

According to preliminary forecasts, in some regions of Russia, the use of carbon dioxide for enhanced oil recovery (EOR) can compensate for the rather high costs of its capture, which account for about 70-80% of the total cost of CO₂ disposal technology, depending on the specifics of a particular project [10].

The CO₂-EOR process, like any other kind of CCUS technology, involves a CO₂ capture operation, requiring a stable and steady stream of carbon dioxide with high purity. A stable CO₂ source is mostly convenient to capture from anthropogenic sources or separated from natural gas with high CO₂ concentration [4]. Despite the significant advantages of CO₂ injection into the reservoir from the surface, the risks associated with the capture, transport and storage of carbon dioxide can significantly reduce the possibility of its use in the processes of enhanced oil recovery and oil production stimulation. In the Russian practice of tertiary mechanisms of hydrocarbon recovery at the stage of water-gas influence there are successful examples of development and wide industrial application on the basis of experimental, theoretical and field studies of highly effective technology of in-situ generation of gas-liquid rim on the basis of carbon dioxide, which allows to effectively regulate the dynamic processes of oil displacement by water [11-12].

3 CO₂-EOR and conventional CO₂ capture technologies

The CO₂-EOR process, like any other type of CCUS technology, involves a CO₂ capture operation, requiring a steady and stable stream of carbon dioxide with high purity content. A stable CO₂ source is mainly convenient to capture from anthropogenic sources or separated from natural gas with high CO₂ concentration [4].

As capture technologies vary greatly depending on the industry in which they are used, more common industries, such as the power sector (coal and gas-fired power plants), are often chosen to analyse the technical and economic components of projects. In the process chain of CO₂ capture and underground storage, the capture process can account for up to 60-70 per cent of the total project cost.

Three main conventional conventional technological methods of CO₂ capture are identified as strategies for major industries: "pre-combustion" capture, "post-combustion" capture and capture by combustion in pure oxygen [13].

In the "pre-combustion" capture process, the carbon monoxide (CO) present in the so-called "synthesis gas", obtained by reforming or partial oxidation, is converted to CO₂ and then separated from H₂ at high pressure. In such energy systems, the final product of combustion is water vapour. In contrast to post-combustion capture, in the "pre-combustion" capture process the separation of the gaseous mixture of hydrogen and carbon dioxide in the second stage of the process is based on physical absorption rather than chemical absorption. Further separation of the stream from hydrogen is not particularly difficult due to the low mass of this gas [1]. "Pre-combustion" fuel conversion processes seem more complex and appear more costly than "post-combustion" methods. However,
circumstances are changing due to high CO₂ concentrations of up to 15-60 per cent by volume and increased pressure, which improves the CO₂ separation capability. This is also favoured by the smaller volume of gas stream treated in "pre-combustion" processes, which is 200-300 times smaller compared to the volumes encountered in "post-combustion" techniques, contributing to the economic viability of the process.

This capture technology is used, for example, by Shell in the refining of oil sands bitumen in the Quest project (Canada) and in the Century Plant project (USA) at the gas processing plant [8]. Since the early 2010s, the Century Plant project has risen to global leadership for its innovative practice of capturing carbon dioxide gases at the pre-combustion stage in a gas processing plant. The method of delivering carbon dioxide in supercritical form has also been unique – it is transported through a pipeline over a considerable distance of up to 260 kilometres. Quest is another popular "pre-combustion" carbon dioxide capture project at the Blue Hydrogen from Methane Unit in the refining and processing of heavy crude oil from Canadian oil sands. The captured carbon dioxide is then stored in an aquifer and can be utilised by injection into the oil sands as part of a combined enhanced oil recovery (EOR) method. Abu Dhabi CCS stands at the forefront as the only "pre-combustion" carbon dioxide capture project in the ferrous metals industry. This project realises a technology in which CO₂ is captured during the direct reduction process of iron using so-called blue hydrogen. The carbon dioxide thus captured is then used as a method for improved oil recovery in the Bab oil field [8].

In "post-combustion" gas stream CO₂ capture processes, systems using mechanical separators and amine-based liquid solvents (amine scrubbers) with a cold solution of monoethanolamine (MEA) are used. The amines used in scrubber systems enter into a stable chemical interaction with carbon dioxide when in contact with the gas stream. Through a heating process, this bound CO₂ is released, allowing the amines to be newly regenerated for further use in the manufacturing process. This method, known as chemical absorption, is typically used in plants with low levels of CO₂ in the exhaust gas, up to 15%, including coal dust and natural gas fired combined cycle plants. Despite the widespread use and understanding of this technology, its key limitations are due to its high energy consumption and significant costs in the carbon dioxide capture stage [14].

Examples of such industrial projects are the capture projects at the Petra Nova (USA) and Boundary Dam (Canada) coal-fired power plants. Thus, in 2017, a consortium of companies in partnership with the US Department of Energy launched the Petra Nova project, which is one of the state-of-the-art "post-combustion" capture projects at a coal-fired power plant. The cost of capture here is about $70 per tonne of CO₂, which has become a price benchmark for subsequent similar capture systems. In turn, the Boundary Dam project in Canada, which has been running since 2014, is the world's first industrial "post-combustion" capture system at a coal-fired power plant, with a capture cost of about $105 per tonne of CO₂ [8].

When using the "oxygen assisted combustion" method, where the process takes place in an environment of pure oxygen rather than air, a more environmentally friendly combustion process can be observed, with CO₂ emissions at 80% of the volume. This is due to the absence of nitrogen in the mixture, and the result is the generation of water vapour, which is not difficult to remove [1, 14]. Nevertheless, this combustion approach, despite its effectiveness in CO₂ accumulation, faces a number of challenges when integrated into existing power plant processes. In addition, practical experience with the application of such systems in industrial applications is still limited, emphasising compatibility issues with conventional power generation methods. Based on the available information, although the use of oxygen in the combustion process is suggested as a way to minimise the need for complex emission treatment systems, the cost of adapting current power plants to the new technology can far exceed traditional methods, such as the use of amine solvents to release
carbon dioxide in "post-combustion" process cycles. As a result, despite references to the application of this technology in the glass industry, approaches based on the fuel oxygen enrichment process are still poorly understood and very selectively applied to reduce CO₂ emissions [15].

4 New promising technological developments for CO₂ capture

In addition to the already existing and widely used CO₂ capture technologies in industry, which have come to us from various related fields and have proven their effectiveness in numerous pilot projects, new promising technologies are currently under development. These innovations are still in the early stages, undergoing laboratory tests and first pilot runs.

The concept of one of the project developments is based on the use of unique membrane filters to clean the combustion flue gases during the combustion process. Constructed from materials such as ceramics and polymers, these filtration systems specialise in the permeation of carbon dioxide molecules [16-17].

Using membrane capture techniques at low pressures, the process favours the permeation of the gas stream through the membranes and further interacts with the liquid absorbent to effectively remove carbon dioxide from it. Thus, the membrane serves as a barrier between the gas and liquid stages where CO₂ removal is ensured due to the unique absorption properties of the absorbent. Such a capture technique opens a new chapter in the evolution of "post-combustion" carbon dioxide capture technologies [16].

The use of membranes at high pressure offers the potential for efficient gas separation without the use of liquid solvent, especially in systems aiming to capture emissions prior to combustion. These membranes are able to trap CO₂ molecules, separating them from other components of gas mixtures due to differences in size or travelling paths [16].

The next method under consideration is based on the application of a technology that involves combustion of fuel in oxygen, and engages the mechanism of chemical loop combustion (CLC). In this mechanism, calcium or various metals serve as carriers of oxygen and heat, travelling between the two reaction zones. The main process is divided into two stages: the first stage is characterised by the release of heat through an exothermic reaction, while the second stage absorbs heat through an endothermic reaction. With the right choice of catalyst, this approach can reduce the temperature and burn the fuel. In addition, using only oxygen instead of air in the combustion process results in a predominantly carbon-containing output stream due to the absence of nitrogen oxides (NOₓ) [16].

Several advanced and breakthrough carbon dioxide capture technologies are mentioned in some literature sources, which are undergoing the implementation process or are at the stage of pilot studies. For example, the process of CO₂ capture from the environment - direct air capture (DAC) technology is reported [18].

From a thermodynamic point of view, DAC technology is very inefficient due to the low concentration of CO₂ in the air, slightly above 400 ppm compared to industrial emissions. It faces significant technological challenges related to absorbent/adsorbent aspects, efficiency and energy costs. Nevertheless, this technology is attractive because it does not require the construction of infrastructure and transport of CO₂ over long distances, as the relative location of the emission source and CO₂ disposal/storage sites is no longer an issue [18, 19].

DAC research in recent years has mainly focused on finding high performance solid and liquid absorbents/adsorbents, as well as prototype demonstrations and technology life cycle assessments. Absorbents and adsorbents are key components of the DAC process system and their performance directly affects the overall cost and efficiency of the process. Thus,
the technological maturity of DAC in general is still low and the application of this innovative solution is in its infancy [20].

Meanwhile, over the past decade, developed countries in Europe have placed great importance on the development and application of DAC technology. Climeworks, based in Switzerland, is the first company in the world to provide air-generated CO₂ to customers. In 2017, the company commissioned the world’s first commercial DAC technology device in Switzerland, achieving a total capture capacity of several hundred tonnes of CO₂ per year. And in 2021, Climeworks built a new plant in Iceland, which has a capture capacity of 4,000 tonnes/year and is now the largest DAC demonstration project in the world. The captured CO₂ is injected to a depth of 700 metres for mineral storage [21].

In turn, in 2015, Carbon Engineering built its first DAC pilot plant using KOH and Ca(OH)₂ solutions as absorbents, and in 2017, the company succeeded in converting air-captured CO₂ into liquid fuels. In 2019, the company started the design and construction of a million tonne DAC demonstration project [22].

One of the new and rapidly developing directions in materials science is the application of flexible metal-organic frameworks (MOFs). These materials are formed by complexed metal ions or clusters of metal ions linked by bridging organic linkers. Their crystal lattices have a well-defined pore structure and large surface area [23-24]. The properties of the dynamic component make it possible to create metal-organic frameworks responsive to external factors such as pressure, temperature, UV light and others. Thus, it is possible to develop a material for efficient CO₂ capture with reversible phase, which will allow the CO₂ capture process to be carried out with minimal cost [25]. Despite the clear advantages of technological solutions, the energy consumption of a potential carbon capture process using MOFs is still relatively high, accounting for 70% of the entire process chain.

In Table 1 we summarise all the carbon dioxide capture technologies considered, listing their clear advantages and technological difficulties of large-scale implementation.

**Table 1.** Advantages and disadvantages of the carbon dioxide capture technologies under consideration.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages over traditional CCU technologies</th>
<th>Technological challenges and disadvantages</th>
</tr>
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<tbody>
<tr>
<td>Pre-combustion capture</td>
<td>- cost savings;</td>
<td>- reduction of work efficiency by up to 20%;</td>
</tr>
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<td></td>
<td>- low volumes of waste and emissions</td>
<td>- change in the structure of the technological process;</td>
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<td></td>
<td></td>
<td>- high costs</td>
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<tr>
<td>Post-combustion capture</td>
<td>- can be combined with operating power systems;</td>
<td>- up to 30 per cent reduction in operational efficiency;</td>
</tr>
<tr>
<td></td>
<td>- low costs</td>
<td>- large volumes of waste;</td>
</tr>
<tr>
<td>Oxygen combustion</td>
<td>- CO₂ is a separate stream;</td>
<td>- high material intensity</td>
</tr>
<tr>
<td></td>
<td>- minimal emissions;</td>
<td>- up to 25% reduction in efficiency;</td>
</tr>
<tr>
<td></td>
<td>- low material intensity</td>
<td>- change in the structure of the technological process;</td>
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<tr>
<td></td>
<td></td>
<td>- high costs</td>
</tr>
<tr>
<td>Membrane technology</td>
<td>- easy operation;</td>
<td>- low degree of gas purification;</td>
</tr>
<tr>
<td></td>
<td>- minimal energy and material intensity;</td>
<td>- low degree of research</td>
</tr>
<tr>
<td></td>
<td>- possibility of application in the area of</td>
<td></td>
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<tr>
<td></td>
<td>decentralised energy sector</td>
<td></td>
</tr>
<tr>
<td>DAC</td>
<td>- flexibility in localisation;</td>
<td>- expensive high efficiency adsorbents/absorbents;</td>
</tr>
<tr>
<td></td>
<td>- minimisation of transport requirements;</td>
<td>- linkage to renewable energy sources;</td>
</tr>
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<td></td>
<td>- solution for dispersed and small-scale</td>
<td>- process engineering;</td>
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<td></td>
<td>emission sources</td>
<td>- scale-up</td>
</tr>
<tr>
<td>MOF</td>
<td>- reduced energy consumption for carbon</td>
<td>- expensive high-performance materials;</td>
</tr>
<tr>
<td></td>
<td>capture</td>
<td>- process engineering</td>
</tr>
<tr>
<td>chemical looping</td>
<td>- CO₂ is a separate stream;</td>
<td>- difficulty of integration into existing technologies;</td>
</tr>
<tr>
<td>combustion (CLC)</td>
<td>- increased combustion efficiency</td>
<td>- low level of research</td>
</tr>
</tbody>
</table>
5 Conclusion

To ensure large-scale and low-carbon utilisation of fossil energy and resources, CCUS technologies are currently seen as the only approach that will continue to play an important role in combating climate change in the future. However, in line with the new goal of carbon neutrality, the positioning of carbon dioxide utilisation technology priorities has changed significantly and the application scenarios for some advanced and breakthrough CCUS technologies have been greatly expanded. CCUS is now a technological challenge that is driving innovation in carbon capture and storage, facilitating the development of new approaches to reducing harmful emissions.

The advantages and disadvantages of the CO₂ capture technologies discussed above can be summarised in the following brief theses.

- The "pre-combustion" technological approach is a method that reduces the volume of gas processed by a factor of 200-300, which contributes to significant savings in resources such as electricity, water and materials. This approach is also characterised by less waste produced and reduced air emissions. However, it is worth noting that it requires significant changes to existing processes, which can lead to a 20 per cent reduction in plant efficiency and increased costs due to the novelty of the process.

- "Post-combustion" technology can be easily integrated into existing energy systems with minimal installation time required. However, this method is associated with a number of drawbacks including a reduction in plant efficiency of up to 30 per cent, increased waste, large water and resource requirements, and the need for significant space requirements.

- The introduction of "oxygen combustion" technology promises to significantly reduce emissions by creating a clean flow of carbon dioxide and minimising the need for materials. But such an innovation is not without its downsides: there may be high implementation costs due to the need to radically change existing processes, as well as a potential reduction in the efficiency of power plants by a quarter, which increases operating costs.

- One promising yet questionable technology is the use of membranes for purification. This approach is inexpensive to implement due to the lack of need for complex equipment, does not require large expenditures on water and materials, and saves on energy costs because it operates without heating. However, there are doubts about the efficiency of flue gas cleaning and whether it can be successfully applied on a large scale due to limited understanding of the process.

- Chemical loop combustion (CLC) is an innovative technology with unique advantages: it produces clean CO₂ without the need to invest in expensive machinery and improves fuel efficiency through the use of catalysts and by reducing the temperature at which the reaction takes place. However, there are challenges in applying this technology: it is not always compatible with existing developments and requires more research to fully understand its potential and limitations.

- Compared to conventional recovery technologies, the localisation of direct capture of CO₂ from air (DAC) is highly flexible: the need for CO₂ transport can be minimised by locating DAC in close proximity to emission sources. Currently, DAC is an immature technology and the cost of the process is still relatively high. The development of efficient absorbents/adsorbents, integration with renewable energy, process design and scale-up are among the most urgent issues to be addressed.

- Reducing the cost of CO₂ capture using flexible metal-organic frameworks (MOFs) is of particular importance to reduce costs for large-scale application of recycling technologies. However, the performance of the presented MOFs cannot yet fulfil the
requirements of practical applications. Further research including the development of a suitable process is needed.

Acknowledgments

The research was carried out at the expense of the grant of the Russian Science Foundation (RSF) № 24-29-00882 "Scientific substantiation of technology for increasing the stability of water-gas mixtures to increase oil recovery while reducing the carbon footprint" (https://rscf.ru/en/project/24-29-00882/).

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