Inżynieria i Ochrona Środowiska 2018, 21(3), 261-271
Engineering and Protection of Environment
https://ios.is.pcz.pl/

p-ISSN 1505-3695
e-ISSN 2391-7253
DOI: 10.17512/ios.2018.3.5

Izabela MAJCHRZAK-KUCĘBA, Przemysław SZYMANEK
Czestochowa University of Technology, Faculty of Infrastructure and Environment
ul. J.H. Dąbrowskiego 73, 42-201 Częstochowa
e-mail: izak@is.pcz.czest.pl

CCU Technologies in the Green Economy

Technologie CCU w zielonej gospodarce

The paper presents the development of CCU (Carbon Capture and Utilization) technology and its significance in the green economy. The focus was on CO_2 utilization technologies with high potential for commercial application. Carbon dioxide captured from coal-fired power plants, cement plants or in other industry sectors offers an alternative source of coal for obtaining fuels, chemicals and materials. The focus of the paper is on the technological, environmental and financial barriers to the implementation of CCU technologies on an industrial scale.

Keywords: **carbon dioxide, utilization, CCU technology**

Introduction

Air pollution has a significant impact on the environment and generates a number of adverse phenomena such as the greenhouse effect. Limitation of the anthropogenic greenhouse gas emissions, including CO_2 in order to counteract climate change is becoming a priority of the initiative in both the EU and all countries of the world. The first global climate agreement signed in December 2015 in the capital of France by nearly 200 countries during the UN climate convention aims to maintain a global average temperature rise at a level substantially lower than 2 degrees Celsius compared to the pre-industrial age and to continue efforts to reduce the temperature rise by 1.5 degrees [1].

This objective can be achieved by reducing the anthropogenic CO_2 emissions, increasing percentage of energy from renewable sources and improving the energy efficiency.

With the requirements regarding the reduction of CO_2 emissions, which are increasing at the subsequent stages of the implementation of the EU's climate policy, more and more industries are obliged to reduce CO_2 emissions. Nowadays, the obligation to reduce CO_2 emissions concerns not only the energy sector but also cement, metallurgy, petroleum and chemical industries. These industries are perceived as significant sources of air pollution with carbon dioxide. Electricity generation, steel production, cement production, and oil production should develop

---

along with reduction of anthropogenic CO_2 emissions and other pollutants into the air.

Due to the growing problems of anthropogenic emissions of CO_2 from transport and other small sources, more and more research concerns the separation of $CO_2$from the surrounding air. It is referred to as air capture because it concerns the direct CO_2 capture from air. The captured pure CO_2 stream can be stored or utilized similar to CO_2 captured from power plants or other industry sectors [2].

It is important that all initiatives aimed to limit anthropogenic CO_2 emissions also contribute to lower emissions of other gaseous pollutants, i.e. NO_x, SO_x, Cl, Hg, which is of great importance to the atmosphere protection. All CO_2 capture technologies include the step of deep cleaning of gas stream from NO_x, SO_x and other pollutants before the main CO_2 separation process. This is also important in light of tightening requirements regarding permissible SO_x and NO_x emissions to the atmosphere.

The problems of climate and environmental changes and activities related to the limitation of anthropogenic CO_2 emissions have inspired the development of CCS and CCU technologies (Carbon Capture and Storage, and Carbon Capture and Utilization). The interest in these technologies results from the need for reduction of huge amounts of CO_2 generated mainly from power plants and combined heat and power plants and also from other industries such as the metallurgy, cement and petroleum industries.

Although CO_2 capture technologies have been essentially developed in the energy sector, the International Energy Agency (IEA) forecasts (relative to the current level) show that nearly half of all operating CCS units will be located in cement plants, steelworks, chemical factories and refineries. The high potential of CCS technology in these industries results not only from significant CO_2 emissions, but also from the fact that many industrial processes generate gas with a high concentration of CO_2, which significantly reduces the costs of CCS technology. An additional argument is also that these sectors have already exhausted the potential of reducing CO_2 emissions by modification of their production processes. Consequently, meeting the emission requirements is possible only through implementation of CCS/CCU technologies [3].

Until recently, the proposed CO_2 capture technologies have been focused mainly on capturing CO_2 with maximum purity at the highest possible recovery rate. The main option proposed for captured CO_2 was to store it, mainly in underground mine voids and coal seams. Despite much research done into these problems and great potential in terms of storage locations, this method generates problems with social acceptance. In recent years, more and more efforts are made to develop technologies in which waste CO_2 captured from power plants or other industries can be converted into carbon for production of fuels, chemicals and various materials. This is consistent with the idea of the green economy based on environmentally friendly technologies since it allows for reduction of greenhouse gas emissions, increasing the use of renewable energy and obtaining effective products based on waste carbon dioxide.

1. CCU technology

In the CCU technology, carbon dioxide, after separation and recovery from coal-fired power plants, can be converted into fuel or chemical compounds suitable for the use in many chemical processes. The idea of the CCU technology is that it is much easier to convert gas than to store it. Such an approach opens up new perspectives and may attract interest from the industry. The key factor in CO_2 utilization is high energy consumption. In order to ensure that the a disposal technology emits minimal amounts of CO_2, the energy needed for the process has to be supplied from renewable sources.

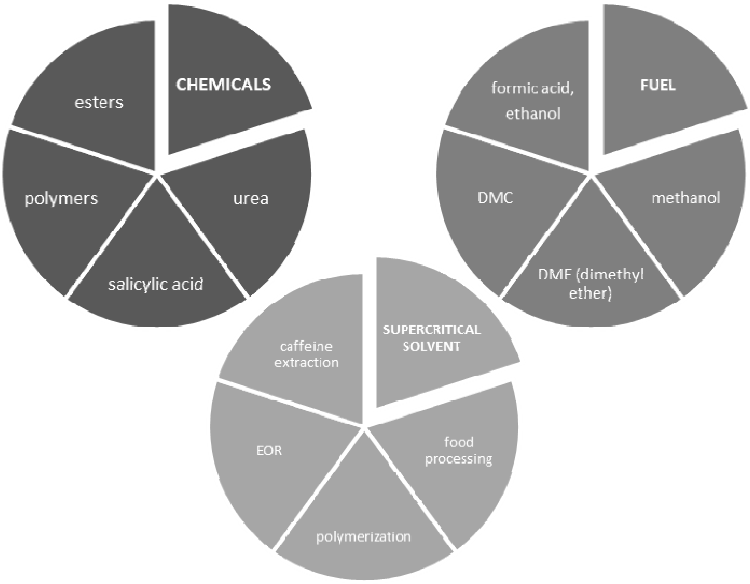

Fig. 1. Chemical utilization of waste CO_2

In general, CO_2 conversion processes can be divided into three main categories: biological processes (in which organisms absorb CO_2 rapidly and use sunlight to produce the final product), chemical processes (in which the carbon-oxygen bond is broken and then carbon is connected with other elements to obtain the final product) and mineralization process (CO_2 reacts with other compounds and is stored as solid carbonates that can be integrated into the final product) [4]. The present paper focuses mainly on chemical CO_2 utilization, especially on chemicals and fuels (Fig. 1).

The important factor in the CCU concept is to develop technologies capable of converting most of industrial CO_2 emissions into useful products with high value added. The attempts are also made to develop technologies that could be used on a large scale. Currently, CO_2 utilization technologies are at various stages of development, ranging from technological readiness levels of TRL 2 to TRL 9, that is, laboratory tests, innovation phase, first industrial production, and readiness for commercialization. However, it should be stressed that most CO_2 utilization tests have been performed on a laboratory scale (technological readiness levels TRL 1-5) and numerous barriers to their further development are yet to be overcome. Table 1 presents the most promising opportunities for carbon dioxide utilization in industrial processes in Europe, including the level of development for a technology (TRL) and CO_2 conversion factor (the amount of CO_2 used per unit of product or used raw material) [5].

Table 1. **Selected opportunities for carbon dioxide utilization in industrial processes [5]**

Industrial process	Application type	TRL	Conversion factor
Lignin production	CO_2 for regulation of pH in alkaline solutions	7-8	0.22 tonne of CO_2 per tonne of lignin
Methanol production	Electrochemical CO_2 reduction	7	1.7 tonne of CO_2 per tonne of methanol
Polyurethane production	CO_2 for production of plastics and fibres	7	0.1÷0.3 tonne of CO_2 per tonne of polyols
Polycarbonate production	CO_2 for production of plastics and fibres	7	0.43 tonne of CO_2 per tonne of PPC
Concreting, concrete blocks	CO_2 for precast concrete	7-8	0.03 tonne of CO_2 per tonne of concrete block 0.12 tonne of CO_2 per tonne of precast concrete
Mineral carbonation	CO_2 reacts with minerals containing calcium and magnesium	7-8	0.25 tonne of CO_2 per tonne of steel slag
Carbonation of bauxite residues/waste	CO_2 for neutralization of bauxite waste	9	0.053 tonne of CO_2 per tonne of red sludge (red mud)
Horticulture	CO_2 for plant growth	9	0.5÷0.6 kg CO_2/h/100 m^2 160 t CO_2/hectare (tomatoes)
Urea production	Production of urea from ammonia and CO_2	9	0.74 tonne of CO_2 per tonne of urea

As can be seen from Table 1, the most advanced technologies of CO_2 utilization include urea production, carbonation/neutralization of waste and the use of CO_2 in horticulture to stimulate plant growth. Furthermore, the highest CO_2 conversion factor can be obtained for methanol production (1.7 tonne of CO_2 per tonne of methanol).

The potential for utilization of carbon dioxide in individual processes in Europe is also important to the choice of a CO_2 utilization technology (Table 2). The highest potential for CO_2 utilization is observed for the construction sector (concrete production) and horticulture.

Since popular CO_2 conversion processes have numerous limitations, new technologies for CO_2 utilization are being developed. In order to intensify the research and establish partnerships for the development and testing of new technologies of CO_2 utilization, numerous contests have been organized, including the International NRG COSIA Carbon XPRIZE awarded by the Carbon Capture and Conversion Institute in Richmond, Canada.

Table 2. **Potential for CO_2 utilization in industrial processes in Europe [5]**

Industrial process	CO_2 utilization (in millions of tonnes per year)
Lignin production	8.4
Methanol production	2.0
Polyurethane production	0.3
Polymer production	8.3
Concreting, concrete blocks	22.5
Mineral carbonation	5.3
Carbonation of bauxite residues/waste	0.2
Horticulture	22.0
Urea production	3.9

The semi-finalists of the contest include teams from Canada, China, India, Switzerland, Scotland and the USA. Among them are companies, universities and non-governmental institutions. The projects include CO_2 conversion in biofuels, toothpastes, nanotubes, fertilizers, and improved concrete. In the final round, contest participants from all over the world present CO_2 conversion technologies that allow for utilization of 200 kg of CO_2 per day [4].

2. Liquid fuels based on carbon dioxide

Carbon dioxide derived from boiler flue gas or other industrial sources can be considered a raw material for production of many synthetic liquid fuels, such as formic acid, methanol, dimethyl ether or ethanol. Many CO_2 conversion technologies have been designed for production of such a variety products. The primary source of energy for these conversion technologies is provided by renewable energy: solar and geothermal energy, that is, the energy which is characterized by low CO_2 emissions. The use of energy from fossil fuels in the processes of CO_2 utilization would result in more CO_2 being released compared to the use of the fossil fuel directly as a fuel.

The main commercial advantage of converting waste CO_2 into a synthetic fuel is to provide an efficient fuel for general use in transport. It is expected that fuels used currently in transport (derived from fossil fuels) will not be able to meet the demands for the years to come. Furthermore, the possibility of using the existing oil infrastructure (transport, distribution, storage, engines and vehicles) is conducive to the use of CO_2-to-liquid fuels if the properties of the liquid fuels are comparable to those of oil or gasoline. The wide application of this technology is also likely to help achieve the goal of low or zero emissions from transport.

Low efficiency and high capital costs of some CO_2-to-liquid fuel technologies represent the key barriers to their implementation. It should also be noted that some technologies will never overcome these barriers and, consequently, they will not be used commercially on a large scale.

Since the main market for the sale of synthetic liquid fuels obtained through CO_2 conversion is the transport sector, alternative transport systems such as electric vehicles powered by energy obtained from renewable sources may also become a barrier.

2.1. Methanol

Production of 'renewable' methanol requires access to CO_2, H_2 and energy. Carbon dioxide can be supplied from power plants or other industry sectors. Water electrolysis yields H_2, which is compressed with captured CO_2, and reacted on the catalyst at a specific temperature and pressure (~ 5 MPa, ~ 225°C) to produce methanol and water. The obtained 'renewable' methanol can be then used as a fuel blend with gasoline (up to 10%) or as a chemical raw material for obtaining e.g. formaldehyde, chloromethane, and esters.

Carbon Recycling International Ltd (CRI) has been producing 'renewable' methanol on a pilot scale since 2007 in a location near Reykjavik, Iceland. The process uses CO_2 from volcanic sources and geothermal energy. H_2 is produced through water electrolysis. Modern water electrolysis systems can reach performance of ca. 65%. According to the CRI patent material, the two gas streams (CO_2 and H_2) are combined and pressurized at ca. 5 MPa before entering the reaction loop, where the mixture is heated to 225°C and then reacted on a catalyst with metal or metal oxide to yield methanol and water, and passed through a counter-current heat exchanger and a condenser in which methanol and water are separated. The gas stream leaving the condenser is connected with new feed gas, and, passing through the heat exchanger, is returned to the reactor. It was estimated that thermal efficiency of the catalytic process amounts to ca. 75%. CO_2 injection can also be used during conventional methanol synthesis. This solution can improve the methanol yield from conventional synthesis by up to 20% [6].

Carbon Recycling International Ltd (CRI) produces approximately 50,000 L of methanol a year, which is sold as a fuel blend under the registered brand name Vulcanol. The use of this blend leads to significantly lower greenhouse gas emissions compared to the use of standard fuels. The development of the technology is supported by the fact that Iceland has very cheap geothermal energy and the access to clean, natural CO_2 from volcanic sources. Iceland also has one of the highest indices of the number of motor vehicles per person (745 vehicles per 1,000 people in 2010), which is conducive to the use of methanol in a fuel blend. Based on the success in 2011, a new pilot plant was opened, producing 5 million litres of methanol per year [6].

Furthermore, Mitsui Chemicals produces 100 tonnes of 'renewable' CO_2-based methanol per year. The process uses waste gas from production of ethylene containing CO_2 but also the accompanying SO_x and NO_x and hydrogen from water photolysis. The methanol obtained is used as a precursor for the production of plastics.

A future goal is to increase the production to 3.7 million tonnes of methanol per year.

Sunfire (Germany) manufactures synthetic fuels for cars based on waste CO_2 in cooperation with Audi. Although the technology is not economical yet, it is being developed, and one barrel of diesel is produced per day to demonstrate its potential [6-9].

2.2. DME

An alternative to fossil fuels (a substitute for fuel for diesel engines or gas cookers) is offered by dimethyl ether (DME) with formula CH_3OCH_3. This compound may also be a substrate in the chemical industry, for example for the obtaining hydrocarbon fuels (gasoline, jet fuel). DME is considered to be a clean fuel of new generation. In external conditions, the gas is colourless and little toxic. Its properties are similar to those of LPG, which makes it possible to use the present infrastructure for commercial purposes. DME has properties similar to methanol, i.e. good low temperature properties, easy transport and low cost of the Cu-Zn catalyst, most commonly used in the process of steam reforming. Due to its high cetane number and good ecological properties, it is considered a very clean fuel for compression ignition (diesel) engines. Its use does not lead to emissions of sulphur oxides and soot particles and is characterized by insignificant emissions of nitrogen oxides, carbon monoxide and unburnt fuel residue. DME can be stored in a liquid form at a moderate pressure of above 0.6 MPa [10].

Dimethyl ether is also recommended as an aerosol propellant because it has zero ozone depletion potential and low global warming potential.

Korea Gas Corporation (KOGAS) performs a direct synthesis of dimethyl ether (DME) from CO_2, O_2, steam and natural gas. DME can be used as a fuel or precursor for other products. Due to similar physical properties, DME is likely to replace LPG and have a large market, especially in Asia. KOGAS proposed a tri-reforming technology for syngas production ($CO + H_2$), which is then converted into DME in a one-step reactor. Production was started from 50 kg per day (2003-2005) to switch later to 10 tonnes per day (2004-2009). The company expects to produce 3000 tons per day [9].

Kansai Electric Power Co. synthesizes DME from carbon dioxide from the Nanko power plant in Osaka in collaboration with Mitsubishi Heavy Industries. DME can be used mainly as a new clean fuel to replace LPG and diesel. Conventionally, DME is synthesized at the first stage from generation of methanol from natural gas and subsequent separation of water from methanol. In the new method, DME is synthesized directly in the reaction of CO_2 captured from a power plant with hydrogen. Such simplification of the synthesis process will allow for a significant reduction of the production plant in the future. Currently, the company strives for increasing synthesis efficiency, reducing production costs and estimating business opportunities [8-12].

2.3. Formic acid

Electrochemical reduction of CO_2 yields formic acid (HCOOH) and O_2. Formic acid is used as a hydrogen carrier. This acid was classified as a liquid fuel because hydrogen is released from the liquid form of the acid only if it is necessary. Electrochemical reduction of CO_2 to formic acid and formate salts is performed by Mantra Venture Group. A pilot installation built in 2013 uses CO_2-containing waste gas from the Lafarge cement plant in Richmond, Canada. Therefore, the chemicals are sold directly from the area where they are produced, without the need for further processing. The pilot installation was designed for processing of 100 kg of waste CO_2 per day [9]. Mantra technology produces formic acid by directly reducing (electrolysis) of CO_2 in water. It requires power supply at the level of 8 MWh/t CO_2, which corresponds to an electrolytic efficiency of 20% if the energy content in the final product (formic acid) is considered.

3. Chemicals and polymers

Production of polyether polyols is a new and promising technology for CO_2 utilization. The use of CO_2 from power plants or other industry sectors reduces the amount of conventional oil-based raw material used to produce polyols, thus replacing the consumption of fossil fuels such as crude oil and gas. The use of waste CO_2 from the power plant as a raw material may allow for extending the range of raw materials in the chemical industry. Carbon dioxide can be an alternative source of carbon in production of polyols. New technologies have an insignificant carbon footprint. Carbon dioxide-based polyols can be used for production of flexible polyurethane foam, used in e.g. upholstered mattresses and furniture, footwear, medical devices and in thermal insulation of buildings and technical equipment. In terms of quality, the foam is characterized by at least the same high standards as conventional material made using only petrochemical raw materials.

In Germany, the technology of obtaining polyurethane based on waste CO_2 is considered very promising. Bayer Material Science (Covestro) partners with RWE, RWTH Aachen University and CAT Catalytic Center to use CO_2 for the production of polyurethane foams. The project called Dream Production was funded by the German Ministry of Education and Science. Flue gas from the power plant is passed through an amine scrubber, whereas CO_2 captured is supplied to a Bayer plant near Leverkusen where polyols are produced, used then for the production of polyurethane foams for mattresses or as insulation materials in buildings. In the latter case, CO_2 emissions are also reduced by minimization of heat losses. Foams containing 10.5% CO_2 are characterized by the same physical properties as those obtained conventionally using petroleum-based materials (fossil materials) and meet all the required standards. Analysis of the life cycle of a product derived from waste CO_2 based on the entire production cycle revealed a 9% reduction in carbon footprint compared to the conventional production of such a product based on carbonaceous fuels. At the next stage, Bayer began commercial production of polyols in Dormagen (foams for mattresses) [8-11, 13-16]. Foam mattresses produced from waste CO_2 are considered ecological products.

Novomer Inc. (USA), converts waste CO_2 from ethanol production into poly (propylene carbonate) and poly (ethylene carbonate) containing up to 50 wt.% CO_2. In terms of costs, the process is comparable with the conventional production of these compounds using crude oil. In 2013, Novomer Inc. announced the first full-scale production of CO_2-based polymers, producing over seven tonnes of propylene polycarbonate (PPC). As a final product, PPC can be characterized by a very long life cycle depending on the application, thus ensuring durability of CO_2 storage. The company produces coatings and adhesives, some of which are used in products sold by Kingspan, a supplier of construction materials.

Furthremore, Jiangsu Jinlong-CAS Chemical Co. Ltd from Taixing, China, produces 22,000 tons of poly (propylene carbonate) and poly (ethylene carbonate) per year, utilizing waste CO_2 from ethylene production. The polymers obtained are used for the production of insulating materials [9].

Polymers partially derived from CO_2 can replace conventional petroleum-based plastics such as polypropylene, polyethylene, polystyrene and polyvinyl chloride.

The use of CO_2 as a raw material for obtaining polymers offers many benefits. Chemicals and materials obtained contain up to 50% of carbon dioxide and are characterized by significantly reduced emissions of carbon dioxide compared to the materials they replace. The conventional infrastructure of the chemical industry can be used to produce the plastics. Polymers offer a wide range of material properties, from rigid solid plastics to viscous liquids [15].

The technology also has many barriers to be overcome to ensure successful development. It is critical to increase the scale and conduct research on new catalysts so that the cost of production of waste CO_2-based polymers is equal to the cost of production of conventional polymers. The purity of CO_2 coming from power plants or other industries is also critical, since the need for additional purification of exhaust gas leads to an increase in polymer production costs [15].

Conclusions

Carbon dioxide can be considered as an alternative source of carbon if it is processed by means of innovative conversion technologies into a useful product, allowing carbon to be recirculated from industrial waste gas generated in the energy sector and other industries.

It should be emphasized that the positive environmental aspect of the chemical valorisation of CO_2 is determined not only by the amount of CO_2 used but also by the avoided CO_2 emissions. This is possible by replacing fossil raw materials with new alternative materials based on CO_2 capture. Technologies for carbon dioxide utilization can therefore support the economy, mostly by increased independence from fossil fuels.

The major barriers to CO_2 utilization include the costs of CO_2 capture, separation, purification and transport to the place of use and limited size of the market for such products. The activities needed to develop new methods of CO_2 utilization include development of effective processes, where boiler gas streams containing CO_2 can be utilized in the presence of other exhaust components.

Acknowledgements

This research was co-financed under the Statutory Research No. BSPB-406-301/11.

References

[1] Energy and Climate Change, IEA, World Energy Outlook Special Report https://www.iea.org/publications/freepublications/publication/WEO2015SpecialReportonEnergyandClimateChange.pdf

[2] Zhang W., Liu H., Sun Ch., Drage T.C., Snape C.E., Capturing CO_2 from ambient air using a polyethyleneimine-silica adsorbent in fluidized beds, Chemical Engineering Science 2014, 116, 306-316.

[3] Abhoyjit S. Bhown, Freeman B.C., Analysis and status of post-combustion carbon dioxide, capture technologies, Environmental Science Technology 2011, 45(20), 8624-8632.

[4] Carbon Capture Journal, Mar/Apr 2017, Issue 56, Future Energy Publishing.

[5] Patricio J., Angelis-Dimakis A., Castillo-Castillo A., Kalmykova Y., Rosado L., Region prioritization for the development of carbon capture and utilization technologies, Journal of CO_2 Utilization 2017, 17, 50-59.

[6] Bocin-Dumitriu et al., Carbon Capture and Utilisation Workshop, Background and Proceedings, 2013.

[7] Bailera M., Lisbona P., Romeo L.M., Espatolero S., Power to gas project review: Lab, pilot and demo plants for storing renewable energy and CO_2, Renewable and Sustainable Energy Reviews 2017, 69, 292-312.

[8] Styring P., Jansen D., Carbon Capture and Utilisation in the green economy, Report no. 51, The Centre for Low Carbon Futures, 2011.

[9] Styring P., Quadrelli E.A., Armstrong K., Carbon Dioxide Utilisation, 1st Edition, Elsevier, 2014.

[10] Górski W., Jabłońska M.M., Eter dimetylowy - uniwersalne, ekologiczne paliwo XXI wieku, Nafta-Gaz 2012, wrzesień, 631-641.

[11] Martin M., Optimal year-round production of DME from CO_2 and water using renewable energy, Journal of CO_2 Utilization 2016, 13, 105-113.

[12] Huang Ch-H., Tan Ch-S., A review: CO_2 utilization, Aerosol and Air Quality Research 2014, 14, 480-499.

[13] Gurtler Ch., Dream Production - CO_2 as Raw Material for Polyurethanes, Bayer Material Science AG, 2013.

[14] Liu S., Wang X., Polymers from carbon dioxide: polycarbonates, polyurethanes, Current Opinion in Green and Sustainable Chemistry 2017, 3, 61-66.

[15] Accelerating the uptake of CCS: Industrial use of captured carbon dioxide, Report Global CCS Institute, 2017.

[16] Mennicken L., Janz A., Roth S., The German R&D Program for CO_2 Utilization - Innovations for a Green Economy, Environmental Science and Pollution Research 2016, 23, 11386-11392.

Streszczenie

W artykule przedstawiono rozwój technologii CCU (Carbon Capture and Utilization), a zarazem jej znaczenie w zielonej gospodarce. Skupiono się na technologiach utylizacji CO_2 o dużym potencjale i możliwościach ich komercyjnego wykorzystania. Ditlenek węgla wychwycony z elektrowni węglowych, cementowni czy innych gałęzi przemysłu może stanowić alternatywne źródło węgla do pozyskiwania paliw, chemikaliów i materiałów. W artykule zwrócono ponadto szczególną uwagę na techniczne, środowiskowe i finansowe bariery wdrażania technologii CCU na skalę przemysłową.

Słowa kluczowe: **ditlenek węgla, utylizacja, technologia CCU**