Sorption methods for capturing carbon dioxide by various sorbents

T S Nechaeva¹, N I Fedorova¹, E V Matus¹, Lei Li², Z R Ismagilov¹

¹Federal Research Center of Coal and Coal Chemistry, Siberian Branch of Russian Academy of Sciences, 18 Sovetskiy Ave., 650000, Kemerovo, Russia
²Institute of Coal Chemistry, Chinese Academy of Sciences, 27th South Taoyuan Road, 030001, Taiyuan Shanxi, P. R. China

E-mail: nechaeva_ts@mail.ru

Abstract. The article discusses the main methods of capturing carbon dioxide used in the processes of cleaning flue gases. The paper presents some schemes for the extraction of CO₂, shows their advantages and disadvantages. The adsorption method for extracting carbon dioxide with commercial sorbents and activated carbons obtained on a coal and plant basis is considered in detail. The characteristics and properties of the main solid sorbents are given. The main indicators of the quality of activated carbons, which affect the efficiency of the extracted gas, have been established. Methods of modification of activated carbons and their influence on the sorption of carbon dioxide have been studied. As a result of the analysis of literature data and taking into account the growth of world energy consumption, it was concluded that carbon dioxide capture is a promising area of scientific research.

Greenhouse gases (CO₂, CH₄, N₂O, etc.) are the main cause of climate change and, as a result, global warming. Carbon dioxide inflicts a serious blow on the environment, as it stays in the atmosphere for a long time. Carbon dioxide emissions are mainly associated with the burning of fossil fuels. By 2040, global energy consumption is projected to grow by 30%. At the same time, 74% of the energy will be provided through the use of fossil fuels, which should be enough for the next 75 years. Due to the high consumption of fossil coal as an energy carrier, it is not possible to reduce CO₂ emissions into the atmosphere. Accordingly, the volume of gas emissions will increase significantly. Therefore, it is necessary to search for methods to reduce carbon dioxide emissions into the environment.

The main methods for capturing carbon dioxide are subdivided into absorption, adsorption, cryogenic, membrane and microbiological [1, 2]. Microbiological and cryogenic processes are not widespread. Figure 1 shows a scheme for cleaning flue gases using absorption by monoethanolamine [3]. The absorption process is carried out at a temperature of 40-60 °C and atmospheric pressure. When equilibrium is reached, the solution rich in CO₂ enters the regeneration, which is carried out at a temperature of 100-140 °C. Then the solvent is cooled down and recycled. This technology is considered effective and is widespread, however, it has several disadvantages, such as equipment corrosion. In addition, due to the high interaction of carbon dioxide and monoethanolamine, the regeneration process takes place with high energy consumption.
A simplified diagram of the adsorption technology for capturing carbon dioxide is presented in Figure 2 [3]. The flue gas is first purified from moisture, sulfur and nitrogen oxides. Then the prepared gas enters the adsorption stage for which solid adsorbents are used, such as activated carbon, zeolites, metal organic frameworks (MOFs), porous polymers, solid materials based on carbonate of alkali metals and amines, carbon spheres [4] and others. After that, the adsorbent goes through the desorption stage, where a gas mixture rich in CO2 is released, which is then compressed under pressure. The advantages of this technology are the high efficiency of carbon dioxide extraction, the low cost of regeneration, and the stability of the sorbent operation. Activated carbons have a high adsorption capacity for CO2 and N2, have a large specific surface area, and also work in humid conditions, unlike zeolites. Also, activated carbons have a lower heat of adsorption than zeolites, so they can be more easily regenerated. Thus, the heat of adsorption by activated carbon at a temperature of 25 °C and 1 bar is 3 kJ, and by zeolites 30 kJ [3].

One of the important indicators of the quality of sorbents used to capture CO2 is the adsorption capacity for carbon dioxide. Basically, the study of the adsorption capacity is carried out both under static conditions and under dynamic conditions.

Under dynamic conditions, carbon dioxide is captured in a special fixed bed reactor, into which a sample of activated carbon is placed and a gas mixture of a given composition is passed through it. In this case, the flow rate of the incoming and outgoing mixture is controlled, as well as the temperature in the reactor. A gas chromatograph is used to determine the amount of sorbed carbon dioxide. An example of an experimental setup for determining the adsorption activity under dynamic conditions is shown in Figure 3 [5].

To study the process of adsorption of carbon dioxide by activated carbons under static conditions, automated devices are used that make it possible to record adsorption-desorption isotherms at various temperatures (25 °C and 0 °C) and pressure up to 1 atm. The adsorption of CO2 under pressure above 1 atm can be carried out by volumetric method on an IMI apparatus (Hiden Isochema). In this case, measurements can be performed in the temperature range from 40 to 160 °C and pressures up to 36 atm.
The adsorption capacity depends on the presence of heteroatoms (oxygen, nitrogen), acidic and basic functional groups on the activated carbon surface, which are involved in the sorption of CO\(_2\). Often, to increase the adsorption capacity for carbon dioxide, activated carbons are modified by including nitrogen groups in their surface [1, 6-8]. For example, activated carbon modified with triethylenetetramine exhibits a high adsorption capacity for carbon dioxide, the value of which is 16.16 mmol/g. However, it should be noted that the operation of such samples in an industrial environment is possible only at elevated pressures of 30-40 bar [9]. The surface modification of activated carbons is considered from the point of view of increasing the selectivity with respect to carbon dioxide, which is part of the flue gases. Since the CO\(_2\) molecule is classified as a Lewis acid, an increase in the selectivity of activated carbons can be carried out by chemical treatment of their surface in order to impart basic properties. This can be achieved by using the modification of activated carbons with oxides of various metals, such as copper, cobalt, nickel, iron and chromium [10, 11].

The most important role in the process of capturing carbon dioxide is played by the microporous structure of activated carbons. To increase the porosity of carbon materials, physical and chemical activation of the feedstock is used. In particular, in [12], the results of a study of the effect of treatment of activated carbon with potassium hydroxide and potassium carbonate are presented. The maximum value of the adsorption capacity for CO\(_2\) reaches 26.0 mmol/g for activated carbon samples obtained by chemical activation with KOH [9]. Moreover, sorbents have a high specific surface area of the order of 2500 m\(^2\)/g.

Zeolites are one of the most widely known type of adsorbents for capturing carbon dioxide. They are natural and synthetic materials and have a microporous crystal framework with a uniform pore size of 0.5-1.2 nm, which form a network of connecting channels important for the separation and purification of gases. The absorption capacity of zeolites is higher than that of
activated carbons. However, for the use of zeolites in industry, an increased pressure of more than 2 atm is required. In addition, the efficiency of using zeolites decreases with increasing temperature and the presence of moisture in the gas mixture. For the regeneration of spent zeolite, it is necessary to use a high temperature [9].

MOFs represent a new class of effective solid sorbents with a high specific surface area up to 10,000 m²/g. When synthesizing MOF, it is possible to regulate the size and shape of the pores. It is possible to increase the selectivity with respect to carbon dioxide due to the formation of open metal areas in the structure of the MOF. In such areas, the CO₂ molecule binds to the pore surface due to the induction of dipole and quadrupole interactions. MOFs have a high adsorption capacity with respect to CO₂ up to 39 mmol/g at a high pressure of 20-50 bar, but a rather low capacity at a low pressure. MOFs are synthesized from inorganic ligands that are expensive. In addition, the MOF lacks mechanical strength during carbon dioxide capture [9].

Materials based on alkali metals exhibit a high ability to capture carbon dioxide [13]. Such materials are relatively inexpensive, highly recyclable and have high prospects in flue gas cleaning processes. The adsorption capacity of metal carbonates is 9.4 mmol/g and 7.2 mmol/g for Na₂CO₃ and K₂CO₃, respectively. It should be noted that the efficiency of using this type of materials is highly sensitive to the temperature regime of sorption.

Also for the adsorption of carbon dioxide, activated carbons are used, obtained on the basis of various plant materials (almond shells, soybeans, eucalyptus sawdust, legumes, coconut shells, sugar cane, palm bark) [6, 14, 15]. The adsorption capacity for CO₂ is 0.62 mmol/g for a sample of sorption material obtained on the basis of coconut shell.

Despite the presence of a large number of scientific articles, it is necessary to expand research work in the field of obtaining and using carbon sorbents based on fossil coals. Sorbents for capturing carbon dioxide must be highly efficient, reliable, and last for a large number of cycles without the use of high pressures and temperatures.

An important point in the adsorption technology of CO₂ capture is that the sorbed gas can be further used in various industries, which makes the adsorption technology using activated carbons economically attractive. Therefore, a large number of scientific studies are currently being carried out aimed at studying the process of sorption of carbon dioxide.

In addition, it is important to note that sorbents of various natures have been studied in the articles, however, the data on the use of sorption materials obtained from fossil coals are limited. The study of the adsorption capacity and selectivity for carbon dioxide of activated carbons based on fossil coals is a promising area of science and is important for solving global warming issues.

Acknowledgments
The reported study was funded by RFBR and NSFC according to the research project №20-53-53018.

References
[1] Yaumi A L , Abu Bakar M Z and Hameed B H 2018 Energy 155 46-55
[2] Hai Alami A, Abu Hawili A, Tawalbeh M, Hasan R, Al Mahmoud L, Chibib S, Anfal M, Aokal K, and Rattanapanya 2020 Science of the Total Environment 717 137221
[3] Rashidi N A and Yusup S 2016 Journal of CO₂ Utilization 13 1–16
[4] Singh G, Ismail I S, Bilen C, Shanbhag D, Sathish C I, Ramadass K Vinu A 2019 Applied Energy 255 113831
[5] Zhang G, Sun Y, Zhao P, Xu Y, Su A and Qu J 2017 Journal of CO2 Utilization 20 129-40
[6] Luo L, Chen T, Li Z, Zhang Z, Zhao W and Fan M 2018 Journal of CO2 Utilization 25 89-98
[7] Yadavalli G, Lei H, Wei Y, Zhu L, Zhang X, Liu Y and Yan D 2017 Biomass and Bioenergy 98 53-60
[8] Raja Shahrom M S, Nordin A R and Wilfred C D 2019 Journal of Environmental Chemical Engineering 7 103319
[9] Yaumi A L, Abu Bakar MZ and Hameed B H 2017 Energy 124 461-80
[10] Hosseini S, Bayesti I, Marahel E, Babadi F E, Abdullah L C and Choong T Y 2015 Journal of the Taiwan Institute of Chemical Engineers 52 109-17
[11] Dissanayake P D, You S, Igala-vithana A D, Xia Y, Bhatnagar A, Gupta S, Kua H W, Kim S, Kwon J-H, Tsang C W and Sik Ok Y 2020 Renewable and Sustainable Energy Reviews 119 109582
[12] Sreńscek-Nazzal J and Kiełbasa K 2019 Applied Surface Science 494 137–51
[13] Ji G, Yang H, Zaki Memon M, Gao Y, Qu B, Fu W, Olguin G, Zhao M and Li A 2020 Applied Energy 267 114874
[14] Ahmed M B, Hasan Johir M A, Zhou J L, Ngo H H, Nghiem L D, Richardson C, Moni M A and Bryant M R 2019 Journal of Cleaner Production 225 405-13
[15] Ogungbenro A E, Quang D V, Al-Ali K A, Vega L F and Abu-Zahra M R M Journal of Environmental Chemical Engineering 2020 1-27