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PURIFICATION OF NATURAL GAS FROM CO_2 BY ADSORPTION METHOD

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ANNOTATSIYA

In addition supplying natural gas to the citizens, we also use natural gas as fuel for vehicles. There are two types of natural gas fuel compressed natural gas or liquefied natural gas. Natural gas is transported by tankers over long distances by liquefaction, as well as through a gas pipeline. To obtain liquefied natural gas, it is necessary to clean the gas CO_2. There is a risk of carbon dioxide freezing during gas cooling. Therefore, it is necessary to find an adsorbent suitable for cleaning CO_2 from natural gas by adsorption. Two different types of adsorbents have been tested: activated carbon and molecular sieve. Adsorption properties of selected adsorbents have been tested and compared.

Keywords

natural gas treatment; adsorption; CO_2 removal.

1.Introduction: There are several options for using natural gas. Fuel for vehicles is one of them. Natural gas can be used as compressed natural gas or liquefied natural gas. Liquefied natural gas is very important for international trade. In the natural gas liquefaction process, the CO_2 must be cleaned before because the CO_2 can freeze during the gas cooling process. Also in the presence of water in natural gas, acid can be formed, and this leads to corrosion of pipes . Removal of CO_2 can be carried out in several ways - adsorption, absorption, and cryogenic separation.

Adsorption separation of CO_2 was chosen for this work. For experiments, two types of adsorbent were used - activated carbon C46 and 13x seolithic molecular sieve. The temperature and pressure were set at the pressure regulation station in the pipeline according to general conditions: 8 ° C and 4.0 MPa.

STG is liquefied natural gas; an odorless liquid cooled to -162 ° C at atmospheric pressure,its volume is 600 times smaller in the state of liquefied gas. Due to its smaller size, if there is no pipeline, STG is needed for long-distance transportation.

2.Adsorption

Adsorption is the phenomenon of capturing molecules of gas, steam or liquid on a solid surface. There are two types of adsorption that work on different principles of binding forces - physical sorption and chemical sorption. In the case of physical sorption, Van der Waals is based on forces, not chemical, and molecules can be adsorbed in more layers. In the case of chemical sorption, the bonds are chemical. The bonds are specific and the molecules are captured only in active centers. Thus, molecules can only be captured in one layer. Unlike physical sorbtion, activation energy is required. The regeneration of the adsorbent can be achieved at different temperatures (Thermo-oscillating adsorption) or at different pressures (pressure fluctuation adsorption) due to different adsorption capacities. PA (low pressure adsorption) technology does not require the use of chemicals-like Amine or other solvents in absorption technology, no heat is used for regeneration (i.e. low energy intensity) and PA units are suitable for large and small technological processes.

3. Experiments

3.1. Adsorption

The purpose of the experiments was to compare adsorbents selected to remove CO2 from natural gas. The transition curves of CO2 were measured with laboratory apparatus. The throughput was set at 300 ml / m3 CO2 in the exhaust gas. Adsorption was carried out at 8 °C and a pressure of 4.0 MPa. The gas mixture used is depicted in Figure 2. 1. Synthetic 13x seolite from Sigma-Aldrich was tested as a molecular sieve and Silo-carbon Activcohle activated carbon C46 adsorbent. The inner surface and pore size of these adsorbents were measured by the BET method at Coulter SA 3100.Table-1 shows the apparatus used to measure the transition curve of CO2. Two cylinders belong to the apparatus. The first of them contains a tested gaseous mixture, and the second contains nitrogen for cleaning the apparatus. There are reducing valves with which the output pressure of 4.0 MPa can be set. Then there are replacement valves for cleaning the device with nitrogen or using a sample gas mixture. The pressure of the inlet gas is measured by a connected manometer as the next part. The gas then flows into an adsorber filled with the adsorbent examined. Adsorber is equipped with valves that close it on both sides, and it a.ga are placed.

	MS 13x	AC C46
Inner surface [m2 / g]	533	1258
Hole size [ml / g]	0.346	0.589

Table 2. The inner surface of the adsorbents and the volume of the pores.

The container is cooled to 8 ° C, then there is a needle valve that lowers the gas pressure in the apparatus to atmospheric pressure. The next part of the device is a manometer, rather than a flow meter, and at the end is an analyzer connected to the computer.

The device is always cleaned first with nitrogen, and then the required gas flow is installed. The flow rate of the gases in each measurement varied slightly due to the low sensitivity of the control element. The current was set at 4.1 l/min in a 13x molecular sieve, and 3.4 L/min for Activated Carbon C46. The samples were activated by heating to 150 °C for 8 hours before measurement. After washing with nitrogen, the model gas mixture is charged to the apparatus. The CO2 content in the exhaust gas was controlled by the FTIR analyzer Nicolet Antaris IGS. When the marginal volume of 300 ml/min CO2 was exceeded, the time and volume of the gas flow was recorded. The experiment continued until the adsorbent was saturated; that is, until the amount of CO2 in the exhaust gas stopped increasing.

Desorption of CO2 from the saturated adsorbent was also carried out. Pressure conductive desorption with low pressure and thermal desorption with high temperature were carried out. During pressure-conducting desorption, the adsorber is connected to a vacuum pump for 1 hour after being lowered to atmospheric pressure. In the case of thermal desorption, saturated adsorbents were recovered at 150 ° C for 8 hours.

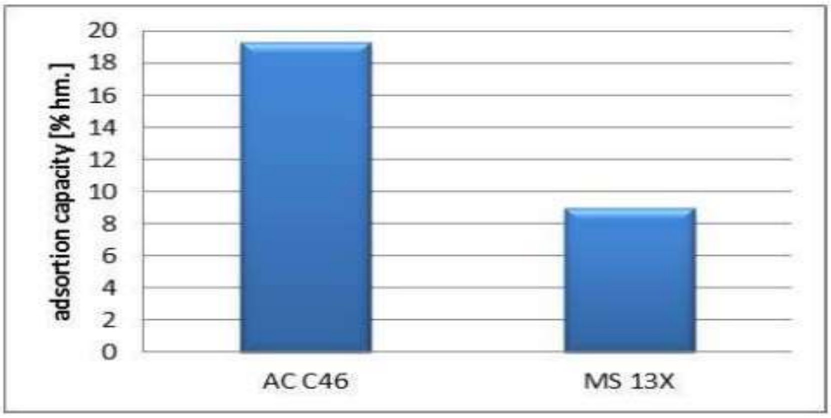

Table 2. The total adsorption capacity at the tested adsorbents by 8 °C

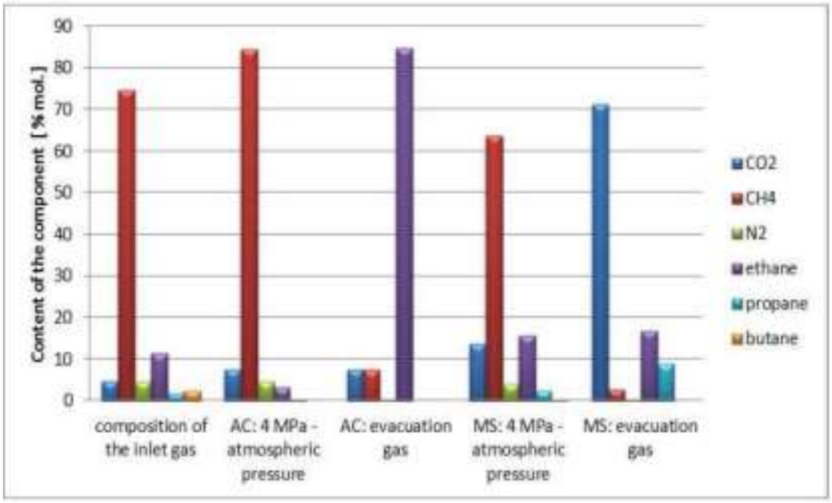

Table -3. Activated carbon C46 and 13X molecular sieve: content of the components in gas extracted by reduction of the pressure from 4.0 MPa to atmospheric pressure and in gas extracted by evacuation.

3.2. Desorption

Desorption of adsorbed gas from a 13x molecular sieve and activated carbon C46 was also tested. In the process of thermal desorption, the adsorber was disconnected from the apparatus, the pressure was lowered from 4.0 MPa to atmospheric pressure, and the adsorbent resumed at atmospheric pressure at 150 °C for 8 hours. In the case of pressure desorption, the ball valves were closed; the adsorber was disconnected from the apparatus and pulled. After lowering to atmospheric pressure, the adsorber was pulled again and then the vacuum pump was connected for 1 hour. The gas obtained by depressurization and evacuation was collected and analyzed in the Hewlett-Packard HP 6890 chromatograph. The resulting mass of adsorbed gas was the difference between the post-measurement weight (adsorbent saturated) and the pre-measurement weight. From the resulting mass, the mass of the gas located in the space between the adsorbent particles was subtracted. This mass value is an important part of the final weight (in this case, about 4 g of gas) of a gas at a pressure of 4.0 MPa.

4. Result

The results of the total adsorption capacity of the AC C46 and MS 3x adsorbents examined are shown in Figure 2. These capacities were determined by dragging the adsorber. This indicates that the adsorption capacity of the 13x molecular sieve was 9% of the weight, and that the adsorption capacity of Activated Carbon was greater than 19 wt%. These results are consistent with BET physical adsorption theory: the inner surface and porous volume of activated carbon C46 are higher than that of a molecular sieve.

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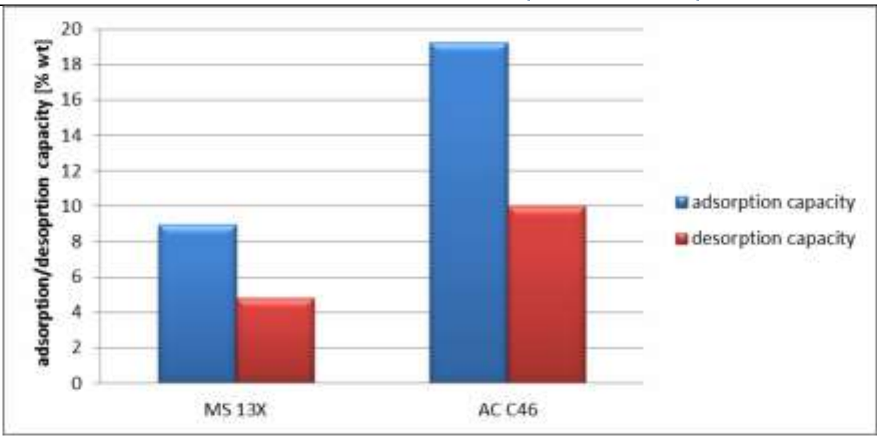

Table 4. Adsorption and desorption capacity – pressure desorption.

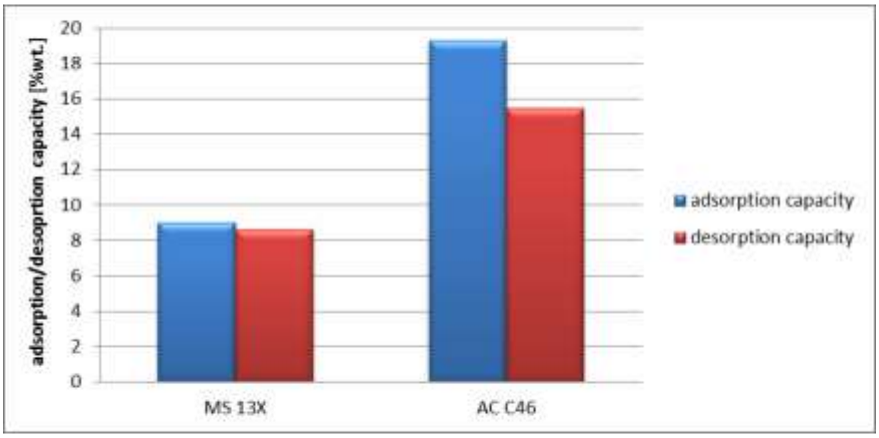

Table 5. Adsorption and desorption capacity – thermal desorption.

This adsorption capacity indicates the overall adsorption capacity of all adsorbed components of the gas mixture; it is not clear if it is only CO2 or if other gases are also adsorbed. An analysis of the adsorbed gas was carried out (it is obtained by reducing the pressure from 4.0 MPa to atmospheric pressure, and then evacuating). These gases were analyzed in a Hewlett-Packard HP 6890 gas chromatograph equipped with FID and TCD detectors. The composition of the gas released by reducing the pressure from 4.0 MPa to atmospheric pressure and the composition of the gas obtained by evacuation is shown in Figure 3 for 13x molecular sieve and activated carbon C46.

The composition of the inlet gas is indicated in the first group of columns. The exact values of the gas content are in Figure 1. The amount of CO2 slightly exceeds the loss of pressure in the gas and evacuation in the case of activated carbon. CO2 is particularly adsorbed and it is released during the reduction of pressure from 4.0 MPa to atmospheric pressure and then during evacuation. In a 13x molecular sieve, the amount of CO2 increases slightly in the exhaust gas compared to the feed gas. It can be assumed that during pressure, a decrease in atmospheric pressure occurs in adsorber, a partial release of CO2 occurs. The dominant amount of CO2 remains adsorbed on the surface of a molecular sieve at atmospheric pressure; CO2 releases adsorbent during evacuation.

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In the case of activated carbon C46, the methane content is slightly higher in depressurization gas than in the inlet gas; methane adsorbs on the surface of Activated Carbon and is released when the pressure drops from 4.0 MPa to atmospheric pressure. Methane is also desorbed during evacuation. As a result of the depressurization of the 13x molecular sieve, the methane content in the gas is slightly reduced compared to the input gas; there is no high adsorption of methane on the surface of the molecular sieve. A small amount of adsorbed methane is released during evacuation.

The amount of nitrogen in the activated carbon depressurization gas is comparable to the amount of nitrogen in the inlet gas, and there is almost no nitrogen in the evacuation gas. On the surface of Activated Carbon, it can be assumed that nitrogen is not adsorbed. In a molecular sieve, the amount of nitrogen in the exhaust gas is compared with the amount in the inlet gas. There is also no nitrogen in the gas from the evacuation of the adsorbent. Thus, nitrogen is practically not adsorbed.

In the case of Activated Carbon, the ethane content in the depressurizing gas is significantly lower than in the inlet gas, and in the evacuation gas it increases slightly. Ethane is adsorbed on Activated Carbon, and it is released during evacuation, but is almost absent during pressure relief. In the case of a molecular sieve, the amount of ethane is higher in the depressurizing gas than in the inlet gas; ethane is adsorbed especially on the surface of the molecular sieve and is released when the pressure drops to 4.0 MPa at atmospheric pressure.

Propane and butane are hardly present in the gas as a result of depressurization and active carbon evacuation; it can be assumed that propane and butane are strongly adsorbed on the activated carbon surface; that they are not released during any pressure reduction. In a molecular sieve, the amount of propane in the gas formed by the loss of pressure is compared with the incoming gas. From evacuation, the amount of propane in the gas increases significantly; propane is adsorbed on the surface of a molecular sieve, and it is released during evacuation. Butane will only be in the inlet gas, there is practically no in the pressure loss gas, as well as in the evacuated gas. Butane is so tightly bound to the surface of the molecular sieve that it does not separate when the pressure drops.

13x molecular sieve and activated carbon C46 were also tested for desorption of adsorbed gas. Pressure desorption results are shown in Figure 4. In the case of pressure desorption, the amount of desorption is slightly 5 wt% for a 13x molecular sieve. For Activated Carbon C46, the amount of desorption reaches 10% by weight. For both samples, this is about half the amount adsorbed. Figure 4 shows that the full amount of adsorbed components cannot be desorbed. Propane and butane, and possibly part of adsorbed CO2, are adsorbed mainly in small layers,

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During thermal desorption, the adsorbent recovered at atmospheric pressure of 150 °C for 8 hours. The results of thermal desorption are shown in Figure 5. In the case of thermal desorption, the amount of desorption reaches 9% of the weight per 13x molecular sieve; this value is close to the adsorption capacity of the molecular sieve. Almost all adsorbed gas is released. The desorption capacity is almost 16% of the weight in activated carbon. Almost 80% weight adsorbed gas is released.

5. Conclusion

Experiments show that activated carbon C46 is a mixture with high adsorption capacity for gas components. Activated Carbon also has a larger pore size and a larger inner surface. However, the ability to adsorb not only contains CO2; mainly propane and butane adsorb. The amount of ethane in the gas from desorption reaches 85% by weight, and the amount of CO2 is lower than 10%. The molecular sieve contains more than 70% CO2 in adsorbed gas. Finally, molecular sieve Activated Carbon has a higher adsorption capacity for CO2 than C46.

Both adsorbents were tested for desorption of adsorbed gases. Almost all adsorbed gases were separated from the 13x molecular sieve by thermal desorption, and almost 80% of the adsorbed gas weighing was desorbed from Activated Carbon C46. Vibration desorption of pressure was not as successful; only about half of the adsorbed gas was released. A 13x molecular sieve is an adsorbent suitable for CO2 from natural gas. CO2 is mainly adsorbed on the surface of a molecular sieve and is also effectively desorbed by thermal desorption. At the same time, activated carbon can be used to remove propane and butane from natural gas.

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