

Sorption of *n*-Alkanes on the Molecular Sieves. I. Description of the Equipment

D. BOBOK, E. KOSSACZKÝ and J. ILAVSKÝ

*Department of Chemical Engineering, Slovak Technical University,
Bratislava 1*

Received October 14, 1969

In this paper a laboratory equipment for determining the break-through adsorption and desorption curves is described. The measuring procedure consists of these actions:

A suitable indifferent gas (nitrogen) is purified and saturated with an adsorbate which is evaporated from a free surface for this purpose. On saturating, the gas is preheated to the adsorption temperature and fed into the adsorber with adsorbent layer. At the outlet of the adsorber, the concentration of adsorbate in the carrier gas is measured continuously by means of a catharometer. After saturation of adsorbent with the adsorbate its desorption starts with an indifferent gas.

The equipment allows the measurements at the adsorption temperatures between 100–500°C for the values of the modified Reynolds numbers referred to the indifferent gas which vary over the range of 1 to 80.

The adsorption on molecular sieves has become a separation process suitable even for the separation of substances from mixtures containing a relatively high concentration of the components. A low mechanical strength of molecular sieves hitherto produced, allows the industrial use only in systems with a fixed layer of adsorbent. For the design of an adsorber, it is necessary to know the data characterizing the adsorption and desorption kinetics in addition to the equilibrium relation adsorbent—adsorbate.

In the prepared series of papers, we shall concern with:

1. The data characterizing the adsorption and desorption kinetics of *n*-alkane on a molecular sieve of the type 5A.
2. The evaluation of original experimental data using the known methods for the calculation of adsorbers.
3. The project of a method suitable for the calculation of an adsorber which is filled with a molecular sieve of the type 5A and used for the separation of *n*-alkane from a mixture with a non-adsorbing component.

This paper is dealing with a laboratory equipment which enables us to determine the break-through adsorption and desorption curves.

Some equipments with similar flow diagrams which, however, permit to work only at laboratory or a slightly higher temperature and with a low passage through the adsorber in such way that the whole flow is passing through the catharometer are described in papers [1–3].

Data for the design of the equipment

The laboratory measurements are made with the globular adsorbent. The effective diameter of particles in particular mesh fractions is within the interval of 0.8–3.0 mm. The density of particles is 1.148 g cm^{-3} . The temperature in the adsorber is 100–500°C, while the pressure amounts up to 800 Torr. The feed into the adsorber: pure hydrocarbon (*n*-heptane) mixed with a non-adsorbing gas (nitrogen, helium). The measurements have to be made within the region of values from 1 to 80 of the modified Reynolds numbers calculated for an indifferent gas. The threshold value of the Reynolds number is 0.90 for the particles with the effective diameter of 0.8 mm, and for the nitrogen gas at 200°C and 780 Torr according to [4].

Description of the flow diagram of the equipment

The diagram (Fig. 1) is characterized by two material flows. The process under investigation takes place in the main material flow while the secondary one functions as a comparative flow through catharometer.

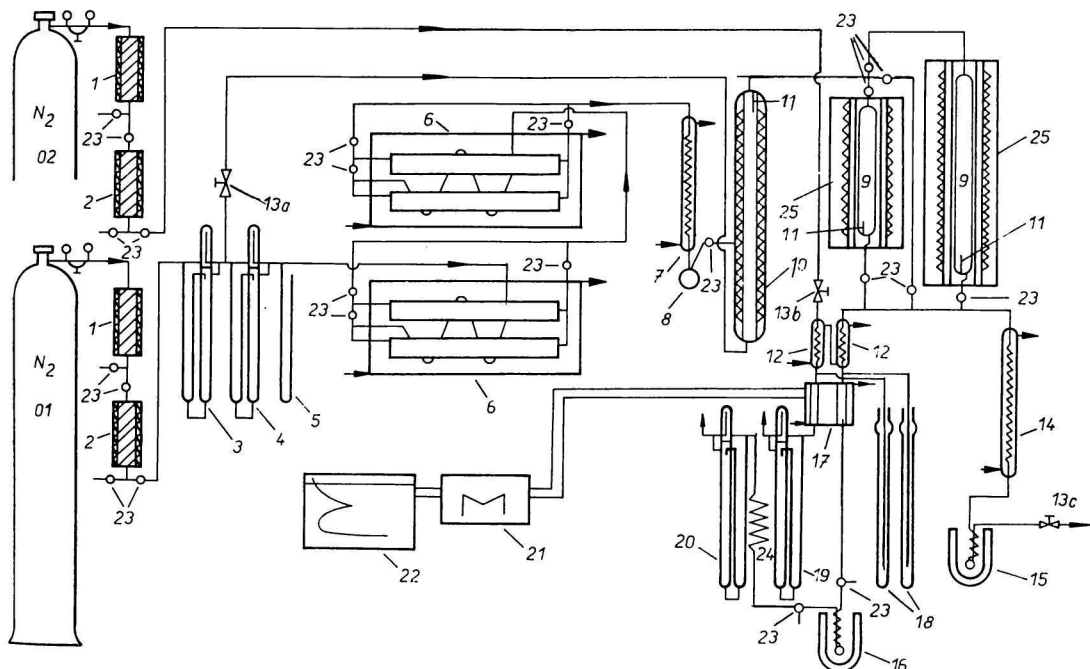


Fig. 1. Laboratory equipment for the measurement of the break-through adsorption and desorption curves.

01, 02 — nitrogen bomb.

1. adsorber filled with Ronge copper; 2. adsorber filled with molecular sieve; 3., 4. flow-meter; 5. U tube; 6. saturator; 7. cooler; 8. collecting flask; 9. adsorber; 10. preheater; 11. tube with the resistance element; 12. capillary cooler; 13a–c. needle valves; 14. cooler; 15., 16. freezing trap; 17. catharometer; 18. manostat; 19., 20. flow-meter; 21. high-resistance bridge; 22. voltage recorder; 23. tap; 24. air cooler; 25. electric furnace.

It is nitrogen which forms the main flow fed into the equipment. Oxygen is removed from this nitrogen flow in adsorber 1 by means of Ronge copper while the humidity is removed on molecular sieve in the adsorber 2. The nitrogen flow entering the equipment is measured with a flow-meter 3, that one passing through the saturator branch 6 being measured with flow-meter 4. The required concentration of adsorbate in nitrogen serving as a carrier gas is controlled by a needle valve 13a which regulates its flow through and out of the saturators certain. The inert gas saturated to a required concentration is preheated to the temperature of adsorption in the preheater 10 and enters the adsorber 9. On getting out of the adsorber the flow of gas is divided into two branches. The main part of gas is passing through the cooler 14, and freezing trap 15 of the first branch into atmosphere. In the second branch (measuring flow of catharometer), the gas passes through the temperature controlled cooler 12, measuring capillary of the catharometer 17, freezing trap 16, heat exchanger 24, and flow-meter 20 into atmosphere. The required flow of gas in the measuring branch of catharometer is controlled by means of the needle valve 13c and manostat 18.

The comparative flow of nitrogen, taken from the vessel 02, passes through the adsorbers 1, 2 where it is purified similarly as the main flow. Pure nitrogen passes through the temperature controlled exchanger 12, comparative capillary of the catharometer, and flow-meter 19 into atmosphere.

Description of the main parts of the equipment

The adsorbers 1, 2 are metallic cylindrical vessels of 80 mm diameter and 400 mm height with external electric heating.

The flow-meters 3, 4, 19, and 20 are made of glass and fitted with exchangeable measuring capillaries. Silicon oil is used as measuring liquid.

The saturator 6 consists of two copper vessels having the shape of lying down prisms (150 × 500 × 30 mm) placed in a temperature controlled bath. These vessels are equipped with a level indicator which also serves as an inlet. The external piping system makes it possible to join the vessels either in parallel or in series connection. Before entering the saturator, the gas is adjusted to the temperature of saturation in a copper tube which is placed in a common temperature controlled jacket.

The adsorbers 9 consist of glass tubes of 16, 25, and 36 mm diameter and 500 or 800 mm height with a sealed glass tube 11, in which a temperature sensitive element is placed.

The preheater 10 consists of a glass tube of 40 mm diameter and 1 m length filled with glass globules and equipped with an external electric heating.

The catharometer 17 as well as the measuring bridge 21 was made in the Research Institute of Petrochemistry in Nováky. The diameter of the measuring as well as the comparative capillary is 4 mm. The filament resistances in heat conductance cell are about 500 Ω. The construction of measuring filaments allows the maximum flow of nitrogen through the capillary to be 30 cm³ min⁻¹. The indication and registration of voltage variation in the measuring bridge 21 is made by means of an electron tube compensation recorder 22 which has the voltage range between 0 and 2 mV.

The furnaces 25 are made of an aluminium block. Each has a hole for an adsorber and regulating transmitter on which a compensation heating is coiled up. The unit thus designed is inserted by means of alundum supports into a metal jacket which is filled with heat isolation. The space between the adsorbers of 16 or 25 mm diameter and the furnace blocks is filled up by aluminium blocks in such way that the clearance between the adsorbers and the aluminium blocks should not exceed 2 mm.

Working procedure

The adsorbers 9 are filled with a weighed amount of molecular sieve and put into the furnaces. The molecular sieve is activated again by heating the adsorbent to 500°C in a stream of pure nitrogen for 2 hours. After activation, the adsorbers are cooled down to the temperature of adsorption, and the required flow of nitrogen in the main branch (outside the saturators and adsorbers) as well as in the comparative branch is adjusted. The flow necessary for the measuring capillary of catharometer is controlled by the valve 13c. The temperature and the flow in the heat conductivity cell having been settled, the heating of filaments is switched on and the zero-line in the recorder is adjusted. By opening the taps for the flow of inert gas through the saturators and adjusting the valve 13a properly, the saturation of nitrogen with hydrocarbon (*n*-heptane) to a required concentration can be achieved. The stable state in saturators is reached in 15–20 minutes. Provided that the gas concentration does not change, the main flow is conducted through the adsorber. The saturation of the molecular sieve is checked by switching the main flow out of adsorber while the zero-line is checked by eliminating the saturators.

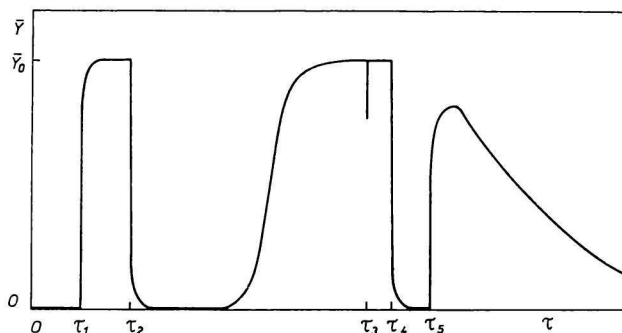


Fig. 2. Dependence of the adsorbate concentration (\bar{Y}) at the outlet from the adsorber on time (τ) effective in measuring the break-through adsorption and desorption curve. 0 — zero-line setting; τ_1 — start of saturation; τ_2 — passing through adsorber; τ_3 — passing outside adsorber (control of the saturation); τ_4 — passing outside saturators; τ_5 — entering of pure inert through saturated adsorber (desorption).

The desorption of adsorbate from the molecular sieve is performed by using a flow of pure nitrogen.

A typical record showing dependence of the adsorbate concentration at the outlet from the adsorber on time, is presented in Fig. 2.

Calibration of the catharometer

Two U tubes filled with the molecular sieve Calsit 5 and inserted into an auxiliary furnace were connected in a parallel way with respect to the freezing trap 16. The activation of molecular sieve was performed in a flow of nitrogen at 500°C. After activation, the molecular sieve was cooled and kept at 270°C (the temperature at which nitrogen does not adsorb) and then weighed together with the U tubes. By connecting the U tubes with the measuring flow of catharometer again and keeping

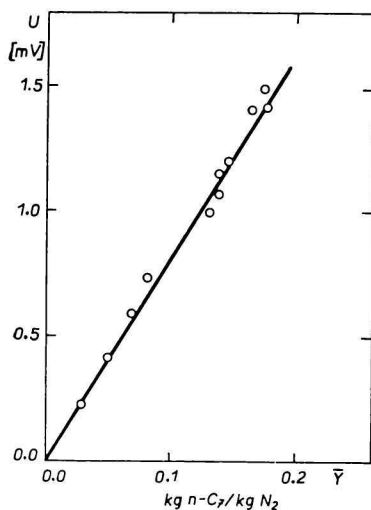


Fig. 3. Calibration curve of the catharometer.

the molecular sieve at 270°C, the equipment was ready for calibration. The zero-line setting and the saturation of gas with the adsorbate was performed in the same manner as in the case of the measurements. At stable concentration of the gas, the measured flow was commutated to go through U tubes. From the known amount of indifferent gas which passed through the flow-meter 20 and from the known increase in weight of the U tubes, the concentration of the adsorbate in the gas could be calculated. Each concentration corresponded to a value on the voltage recorder. By suitable selection of the concentrations, the individual points of the calibration curve were obtained. Fig. 3 represents the calibration curve of the employed catharometer for the system nitrogen—*n*-heptane, corresponding to the temperature of catharometer 20°C, to the flow rate through the capillaries of the cell 25 cm³ per minute and to the heating current 16 mA.

References

1. Campbell M. L., Canjar L. N., *J. Chem. Eng. Data* **7**, 414 (1962).
2. Masamune S., Smith J. M., *Amer. Inst. Chem. Eng. J.* **11**, 41 (1965).
3. Convers A., Defives D., *Rev. Inst. Fr. Pétrole Ann. Combust. Liquides* **20**, 1720 (1965).
4. Kossaczky E., Surový J., *Chemické inžinierstvo I. (Chemical Engineering I.)* P. 187. Slovenské vydavateľstvo technickej literatúry. (Slovak Publishing House of Technical Literature.) Bratislava, 1963.

Translated by R. Domanský