

## Auto-freeze drying by zeolites

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Combining the processes of freezing and drying by means of adsorption with dehydrated zeolite was proposed as a new auto-freeze drying process. This work describes the changes of temperature and mass of the dried product (carrot) and of the adsorbent (zeolite Na-A) during the auto-freeze drying process and the influence of different factors on them. Based on the analysis of the changes of the water states in both the product and the adsorbent, a strategy for harnessing the full adsorption capacity of the zeolite and significantly reducing of the reaction time was suggested. The zeolite freeze drying system works effectively using mainly low-temperature heat and could be functioned by solar or waste heat. The system gives opportunity to recuperate and reuse the heat flows to further enhance of energy effectiveness.

**Keywords:** auto-freeze drying, zeolite Na-A, water state, energy effectiveness.

### INTRODUCTION

The freeze drying produces the highest quality end output for heat-sensitive products compared to other drying methods. Due to the low temperatures (below 0 °C) required for the process, the tastes, as well as any nutritive qualities of the products, are retained. The separation of water is achieved by the sublimation of ice, through which the structure, the form, and the size of the tissue are conserved. The porous structure of the dried product permits its quick rehydration [1–3]. However, the freeze drying is also the most expensive process compared to other drying methods due to high capital and processing costs, as well as its significant duration.

The freeze drying can be carried out in vacuum [1] or in a suitable atmosphere [4]. With contemporary technology, sub-zero temperatures and removal of the vapor are ensured by refrigerating machines [1]. In literature, vacuum systems with removal of the vapor from pre-frozen products through adsorption have been described [5, 6], but have never been developed. An atmospheric freeze drying system with silica-gel as adsorbent has been described by Rahman and Mujumdar [7].

Zeolites are the most effective sorbents for deep drying of gases and liquids [8, 9]. They are capable of drying solid products through contact reactions [10, 11] or air dehumidification by adsorption [12].

Tchernev [13, 14] has first shown that the sorption properties of zeolites are very effective in adsorption cooling and this led to the creation of various freezing, heating, cooling and conditioning systems, driven by low temperature heat such as solar heat or waste energy. Unlike the other solid adsorbents, zeolites adsorb actively even at very low partial pressure of the adsorbate and at relatively high temperatures [8]. In the zeolite-water adsorption systems, cooling is obtained through evaporation of water in the evaporator. When the water molecules of a water-containing product enter the vapor phase, they preserve a significant amount of the latent heat of evaporation (2447 kJ/kg water) and thus, the temperature of water is reduced to the freezing point. Then, the cooling continues at the expense of the sublimation of the ice.

Kirov and Kirov [15] use this effect in an auto-freezing adsorption dryer with an extremely simple construction and maintenance. A prototype device with natural zeolite (clinoptilolite) activated at 400 °C achieves cooling to –25 °C with high drying rates. In later publication [16] the behavior of the freeze dried product and the sorbent (zeolite A) has been studied.

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In this work, we present an auto-freezing zeolite system and describe the results of its trials in the one-stage freeze drying of carrot tissue. The influence of different factors on the temperature of the product and on the kinetics of the drying are taken into consideration as well. Based on the analysis of the change of the water state in both the product and the adsorbent, a two-step process is proposed with the aim of strategically utilizing the full adsorption capacity of the zeolite and the maximal reduction of the reaction time.

## MATERIALS AND EXPERIMENTAL EQUIPMENT

As a model product, an orange carrot from a local market was used. It was cut into ribbons thick 0.3–0.5 mm, wide 3 mm and long 25–120 mm, without further treatment. By drying at 105 °C to a constant mass, a dry residue of 12–13% of the initial wet product is obtained. As adsorbent, Na-A zeolite (manufactured by Zeochem), in the form of pills, with a diameter of 2–3 mm was used. The zeolite was activated in an electric furnace for 1.5 h at 350 °C and cooled to room temperature in a closed vessel, the zeolite lost 22.0 mass% upon thermal activation.

A scheme of the equipment for auto-freeze drying experiment is shown on Fig. 1. The adsorber is a cylindrical glass bottle with an inner diameter of 70 mm and a height of 120 mm. Three glass tubes used to measure the temperature of the sorbent are welded at a distance of 20, 60 and 95 mm from the bottom of the glass equipment. This gives the possibility of monitoring the average temperatures of

three layers 40 mm apart from each other: upper ( $t_u$ ), middle ( $t_m$ ) and bottom ( $t_b$ ). The sublimator is an Erlenmeyer flask with a welded tube for a thermometer 15 mm from the bottom. The two vessels are connected by a glass tube through a vacuum valve ( $v_1$ ) with aperture of 8 mm. Through a second valve ( $v_2$ ), the system is connected to the vacuum pump (Labortechnik, Ilmenau), with end pressure 67 Pa and a capacity of 2.5 cubic meters per hour.

Digital thermometers with a precision of 0.1 °C and electronic balance with a precision of 0.1 g were used.

## RESULTS AND DISCUSSION

The driving force behind the drying process is the difference in partial pressure of water in the environment and the moisture pressure in the product. This difference reaches magnitudes triggering the auto-freezing of the product in the vacuum system. The vigorous adsorption of the water vapors from the zeolite maintains the difference long enough and the drying continues at the expense of the sublimation. The degree of freezing is regulated by a multitude of factors, namely the pressure in the system and the state of the water in both the product and the zeolite.

### One-stage experiments

*Procedure.* 45 g of product are loaded in the sublimator immediately after their grating at room temperature. The adsorber is loaded with 330 g dehydrated zeolite, activated in an electric oven in a layer thick of 1.5–2 cm at a heating rate of 10 °C/min and kept 30 minutes at 250 °C. The sorbent is cooled to 150–160 °C, after which is reintroduced in the adsorber and put into vacuum in order to prevent the sorption of nitrogen from the air at lower temperatures. The cooling zeolite adsorbs the remaining nitrogen and oxygen molecules in the chamber and the pressure drops by one order of magnitude. The sublimator is joined with the system and the product is joined with the adsorber after 1–2 minutes of vacuum pumping. The cooling of the product begins during the vacuum pumping and is accelerated after the junction to the adsorber, which acts as an adsorption pump.

The temperature of the product and the sorbent are constantly monitored during 12 hours. The mass of the product and of the zeolite is recorded both at the beginning and at the end of the experiments (continuously during two of the experiments).

The conditions of four experiments are: In experiment 1 (exp. 1), the adsorber is cooled down and the sublimator is heated by the surrounding

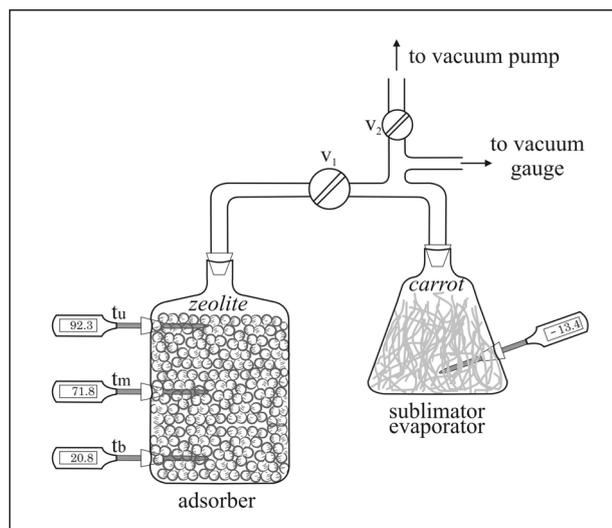


Fig. 1. Experimental equipment used for vacuum freeze drying.

air. In other runs, the sublimator is heated with a 100 W infrared lamp (exp. 2) or insulated with a layer of expanded vermiculite thick 3 cm (exp. 3). In particular cases the adsorber is cooled with filter paper jacket immersed with cooled water (exp. 4). The data about the four experiments are provided in Table 1.

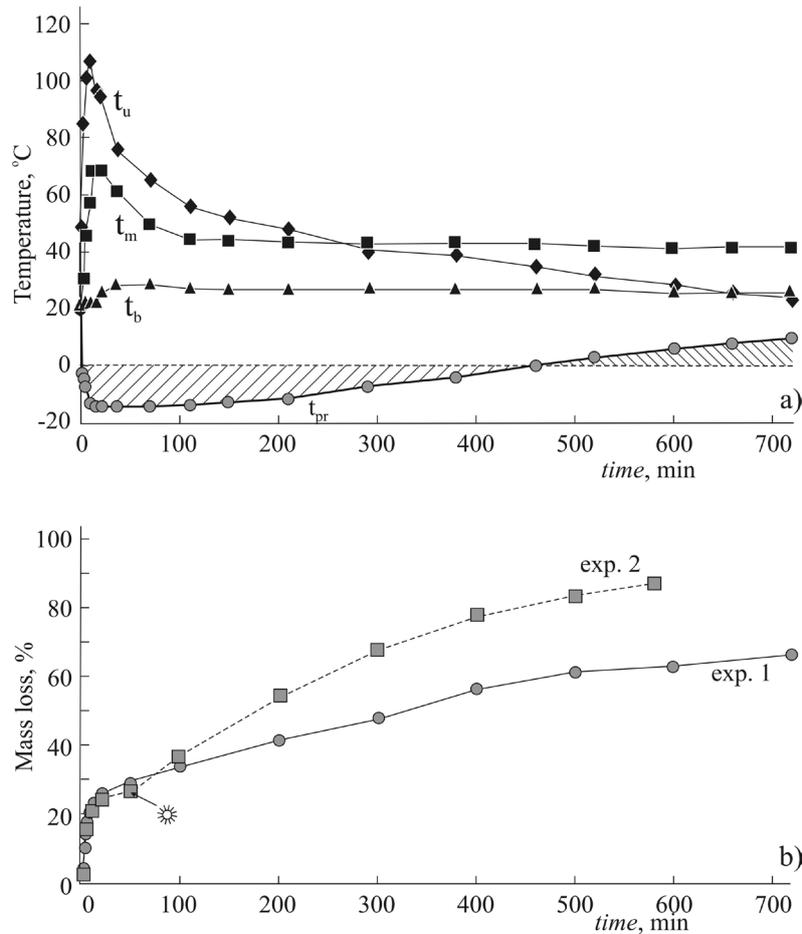
The changes in temperature in the sublimator and the adsorber in experiment 1 are given on Fig. 2a. In this experiment there is only spontaneous heat exchange with the surrounding air. In the first minutes, because of the vigorous evaporation of the water from the carrot, the temperature drops fast. The product freezes for two minutes and reaches  $-14\text{ }^{\circ}\text{C}$  at the 14<sup>th</sup> minute. Meanwhile, the adsorption of the water vapor causes the heating of the surface layer of the sorbent to over  $100\text{ }^{\circ}\text{C}$ . In the following hours, the temperature in the sublimator slowly rises and reaches  $0\text{ }^{\circ}\text{C}$  after 8 hours and  $10\text{ }^{\circ}\text{C}$  after 12 hours. During this period, the temperature of the surface layer of the zeolite decreases at the room temperature. The adsorption continues in the deeper layers and they remain above the room

temperature until the end of the experiment. The weighing of the product and the sorbent at the end shows that the carrot has lost 66.2% of the initial mass, and the mass of the zeolite has augmented by just as much adsorbed water.

The kinetics of the drying can be seen on the gravimetric curve in Fig. 2b. On the curve of exp. 1 there are three segments: steep, declining and a final, almost horizontal. In the steep area, 1/4 of the water from the carrot evaporates. In the first 10 minutes the rate of the dehydration is more than 2%/min and in the following 10 minutes – around 1%/min. In the declining area the dehydration rate constantly decreases to average 0.08%/min for the following 6–8 hours. Finally, the drying ceases, its rate drops under 0.03%/min. In exp. 2, from the 75<sup>th</sup> minute the sublimator is heated with an infrared lamp which moves from 60 cm from the bottom to 30 cm from it at the end of experiment. One can see, that the introduction of heat activates the drying process – the curve become steeper and the product is fully dried after 570 minutes. The product, however, stays frozen only 145 minutes and reaches  $36.6\text{ }^{\circ}\text{C}$

**Table 1.** Comparison of the results obtained in one-stage (experiments 1, 2, 3 and 4) and two-stage freeze drying (experiments 5-1 and 5-2)

Experiment No	1	2	3	4	5-1	5-2
	Extreme temperature and time to reach it, $^{\circ}\text{C}/\text{min}$					
Product	$-14.1^{\circ}/14'$	$-14.6^{\circ}/16'$	$-14.6^{\circ}/30'$	$-15.4^{\circ}/10'$	$-11^{\circ}/11'$	$-16^{\circ}/17'$
Sorbent (upper)	$107^{\circ}/10'$	$115^{\circ}/3'$	$110^{\circ}/10'$	$97^{\circ}/7'$	$78^{\circ}/13'$	$68^{\circ}/17'$
Sorbent (middle)	$68^{\circ}/15'$	$77^{\circ}/16'$	$73^{\circ}/20'$	$92^{\circ}/10'$	$84^{\circ}/77'$	$32^{\circ}/90'$
Sorbent (bottom)	$26^{\circ}/36'$	$37^{\circ}/260'$	$29^{\circ}/720'$	$25^{\circ}/30'$	$32^{\circ}/95'$	$24^{\circ}/170'$
	Time to reach $0\text{ }^{\circ}\text{C}$ in the product, min					
	460	145	does not reach	540	390	95
	Temperature in the end of experiment, $^{\circ}\text{C}$					
Product	9.6	36.6	$-2.2$	6	2	19
Sorbent (upper)	22	27	29	18	37	31
Sorbent (middle)	42	38	36	22	44	26
Sorbent (bottom)	26	31	30	20	32	21
	Duration of the experiments, min					
	720	570	720	720	420	300
	Mass loss in the product, %					
	66.2	87.1	64.0	74.7	56.2	87.3
	Degree of filling, % from maximum sorption capacity					
	41.3	54.0	39.7	46.4	94.9	34.3



**Fig. 2.** a) Temperature of the product ( $t_{pr}$ ) and of three levels of the sorbent ( $t_u$ ,  $t_m$  and  $t_b$ ) during experiment 1; b) mass loss of the product during experiments 1 and 2. The turning on an infra-red lamp is marked with a star.

by the end of the experiment (Table 1). As could be expected, the insulation of the sublimator (exp. 3) has an influence mainly on the frozen state's duration and the drying rate close to those in exp. 1. Cooling the adsorber (exp. 4) causes a decrease in product temperature, thus increase of the time spent of a frozen state (Table 1). As one can see, the application of various effects enables control over the drying conditions. Furthermore, each of those can be applied at given moments of the process regarding the features of the drying product.

As can be seen (Fig. 2b), the rate of drying almost diminishes to zero, even though the sorption capacity of the zeolite is half used. The cause of this is that during the drying process, the states of the product and the sorbent continuously change – the channels of zeolite structure are filled with water molecules and the product is dried more and more, a dry crust is formed, which hinders the diffusion of the water vapors. Analysis of the evolution of

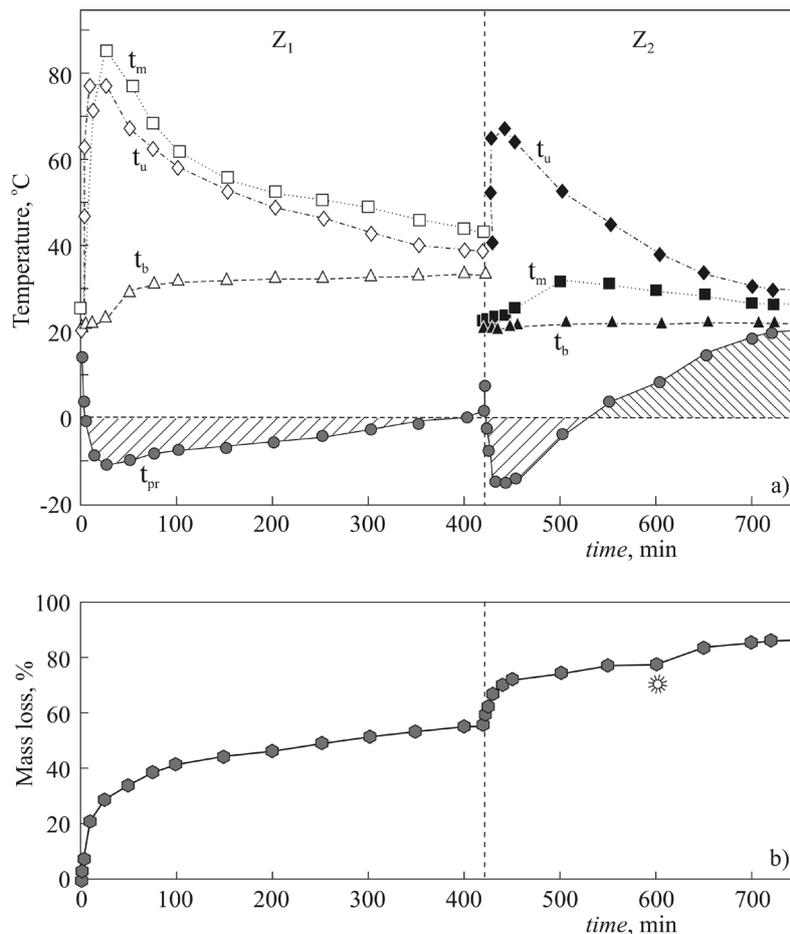
the state of the water in the product and zeolite during the experiment showed a significant discrepancy [17], which influences the effectiveness of the drying process. The weakest bonded moisture of the product is adsorbed at the most active sorption sites in the zeolites, while the strongest bonded water should be evaporated under influence of weakly active centers. A significant improvement to the efficiency of the process could be made by performing the process in the backward flow – to adsorb low-bond product moisture on less active adsorption places in the zeolite and the strongly associated – on the most active places. Unfortunately, this process is technically difficult to perform in the adsorption drying of solid products. A harmonization of the water state of both product and zeolite has been proposed by the application of a two-stage drying process, which provides full consumption of the adsorption capacity of the zeolite, maximal drying of the product and a reduction of duration of the drying cycle by 2 times [17].

## Two-stage experiment

**Procedure.** The used equipment is the same as described above, but with a larger sublimator (400 ml flask) loaded with 80 grams of grated carrot. At the start, 330 g of zeolite are activated up to 250 °C. After the activation, the zeolite is used in a preliminary stage to dry the product during 40 minutes. After that, the partially dried carrot is replaced with a freshly grated carrot and the adsorber is cooled to room temperature. This is the starting point of the two-stage cycle. In the first stage, the zeolite has already used 1/3 adsorption capacity, but due to the large content of free water in the fresh carrot, the product freezes spontaneously and stays frozen for the next few hours, while the sorbent reaches upwards of 90% of its capacity. In the second stage the zeolite is changed with a freshly-activated batch, which adsorbs the remaining strongly-bounded moisture in the product. The dried product is then changed with a fresh one and a new cycle can begin with the partially used zeolite.

The results from a two-stage experiment are given on Fig. 3 and Table 1 as well. In the first stage (exp. 5–1), the middle zeolite layer plays the main role, as the upper layer has already used a part of its capacity in previous stage (Fig. 3a). The temperature of the bottom layer increases, because it also adsorbs. The gravimetric curve (Fig. 3b) has a steep beginning section and then gradually a smooth bend. In these stages the carrot loses 45.0 g water, which is 56.2% of the initial mass of the product, and the zeolite (sown as  $Z_1$ ) uses up more than 90% of its sorption capacity.

The process is reactivated (exp. 5–2) after the change of the adsorber with fully dehydrated zeolite (sown as  $Z_2$ ): the product freezes again for about one hour, and another steep area can be seen on the gravimetric curve. Thus, after 10 hours of drying the product loses 80% of its mass. The full drying is achieved by heating the sublimator with an infrared lamp (to 27 °C) for two more hours (Fig. 3b). In the second stage,  $Z_2$  adsorbs 24.6 g water or 34.3% of the capacity and can still dry out partially a second portion of fresh carrot.



**Fig. 3.** a) Temperature of the product ( $t_{pr}$ ) and of the sorbent ( $t_u$ ,  $t_m$ ,  $t_b$ ) during a two-stage experiment; b) mass loss of the product during drying with two adsorbents. The turning on an infra-red lamp is marked with a star.

The results from the two-stage experiment confirm the conclusions from the two-stage contact drying [17]: full consumption of the sorption capacity of the zeolite, drying to a maximal degree (when needed) and reduction of the drying process duration.

*Dried product.* A SEM photograph of the dried carrot is shown on Fig. 4. According to literature data for freeze dried carrot [3], the preservation of the cellular structure is very well achieved, with big and regular pores. After rehydration the carrot has an odor and taste almost identical to the original. The fully dried product keeps the orange color, the form and the dimensions of the bands of carrot. The dried product is very hygroscopic.

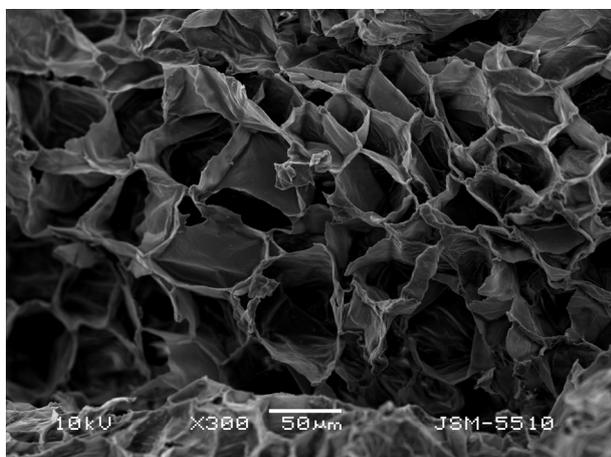


Fig. 4. SEM photography of a freeze dried carrot (exp. 2).

*Heat flows in the zeolite freeze drier.* There are two heat inflows in the system: (i) to dehydrate (activate) the zeolite at a temperature of 200–250 °C and (ii) to provide the latent heat of sublimation and evaporation with a temperature of 30–60 °C. Unlike the conventional freeze driers, which use only electric energy, the zeolite installations can use a number of other heat sources, including solar and waste energy. In these cases, only the vacuum pump is powered with electricity, for no more of 10–12 minutes in drying cycle.

Heat is produced in three heat outflows: (i) the condensation and cooling of water vapor, produced by the activation of the zeolite; (ii) the cooling of activated zeolite from 250 °C to room temperature and (iii) the heat of adsorption of water vapor in zeolite.

Each of the three heat outflows can be used to deliver latent heat for sublimation/evaporation in

the product, but the first and third sources are more fitting to this end. Moreover, as was proved, the removal of the adsorption heat from adsorber enhances its effectiveness. The temperature of activated zeolite is high enough so that the heat outflow can be used for preheating the next portion of adsorbent.

## CONCLUSIONS

The zeolite freeze drying system ensures fast auto-freezing and full drying of water containing products matching the high standards set by the industry demands, even in a device with extremely simple construction and very limited maintenance. The temperature of the product and the kinetics of the drying process can be influenced by the introduction of heat, by insulating the evaporator, cooling the adsorber or pre-freezing of the product, along with other methods, which enable the process to switch between specific customer expectations with ease.

On the basis of the analysis of water states in the product and zeolite, a two-stage experimental scheme providing the full use of the sorption capacity of the sorbent and a steep reduction in cycle duration is suggested. The dried product has a well-preserved cellular structure, high pore content and can be reverted back to the original state with quick rehydration.

The zeolite freeze drying systems can be driven by low-temperature heat, such as waste or solar energy, since the vacuum pump only works for less than 2% of the drying process duration. The system offers ways to recuperate the heat outflows and reach high energy efficiency.

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## САМО-ЗАМРАЗИТЕЛНО СУШЕНЕ СЪС ЗЕОЛИТИ

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(Резюме)

Предложен е нов подход за само-замразително сушене посредством комбиниране на процесите на замразяване и сушене чрез адсорбция с дехидратиран зеолит. Тази работа описва промените в температурата и теглото на изсушения продукт (морков) и на адсорбента (зеолит Na-A) по време на процеса на сушене чрез само-замразяване и влиянието на различни фактори върху него. Въз основа на анализа на промените в състоянието на водата както в продукта, така и в адсорбента беше предложен подход за оползотворяване на пълния адсорбционен капацитет на зеолита и значително намаляване на реакционното време. Системата за само-замразително сушене със зеолит работи ефективно предимно с нискотемпературна топлина като може да функционира със слънчева или отпадъчна топлина. Системата дава възможност за възстановяване и повторно използване на топлинните потоци за по-нататъшно повишаване на енергийната ефективност.