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PYROLYSIS REGENERATION OF ACTIVATED CARBON USED FOR GLYCERIN PURIFICATION

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In this work, we investigated granular activated carbons Norit 1240 (AC) – initial and spent (SAC) with adsorbed impurities after purification of technical glycerin and subsequent washing with water. The aim of the work was to establish the optimal conditions for the thermal regeneration of AC at the pyrolysis unit and to quantify the adsorbed impurities in the SAC using thermogravimetric analysis (TGA). For all AC samples, the specific surface area (S), adsorption activity on iodine and mass fraction of moisture were measured. It was established by the TGA method that water is released in the temperature range of 20 – 180 °C, and glycerin – 180 – 400 °C. Spent AC contains up to 31.3 wt. % H_2O and up to 37.3 wt. % $C_3H_5(OH)_3$. The pyrolysis reactor was used for the regeneration of SAC samples. It was shown that after the reactivation of SACs, their specific surface area is restored to 45-94% of the initial one. There is a weak correlation between S and iodine number, R=0.64. Adsorption activity for iodine and S increase in the same row ACspent > ACregenerated > ACinitial. As a result of regeneration, activated carbons suitable for reuse were obtained.

Key words: *spent activated carbon, thermal analysis, regeneration, pyrolysis reactor*

Introduction

Glycerin, the simplest triatomic alcohol $C_3H_5(OH)_3$, is a product of the multi-ton chemical industry. It is used in paints, food, medical, textile, paper, leather, tobacco, agriculture, detergents and cosmetics, plastics such as polyurethanes, glyphthalic, alkyd and epoxy resins [1].

A reliable way to purify glycerin from impurities is their adsorption using activated carbon (AC) [1 – 3]. However, after prolonged usage, adsorption capacity of the resulted spent AC (SAC) reached saturation which affects its adsorption performances [3]. Reactivation can be carried out by various routes which include thermal reactivation (in the presence of steam/CO_2), chemical reactivation (treated with different chemicals e.g. KOH, NaOH, $ZnCl_2$, H_2SO_4) and bioreactivation (using microorganisms) [2 – 4].

In this work, the adsorption capability of SAC was restored by thermal reactivation in a pyrolysis reactor. Thermogravimetric analysis was used for the quantitative and qualitative evaluation of adsorbed impurities in the spent adsorbent. The presented material is a continuation of the general research direction of the laboratory of oxide nanocomposites of the Chuiko Institute of Surface Chemistry regarding the synthesis and characterization of carbon adsorbents [4 – 10].

Materials and methods

In this work, we investigated granular activated carbons Norit 1240 – initial and spent with adsorbed impurities after purification of technical glycerin. ACs were purchased from LLC "Ukrhimresurs", Ukraine. The numbering and characteristics of AC samples are given in the table.

Thermogravimetric analysis of AC samples was carried out in air using a Q-1500D derivatograph (Hungary) with computer data recording. The heating rate was 10 °C/min, the weight was 0.15 g.

The specific surface area of the samples was measured by the chromatographic method of low-temperature adsorption of argon at -196 °C [11]. The essence of the method is that the experimental samples are analyzed in identical conditions to the standard sample with the known and stable for a long time specific surface. In this case certified reference material BAM-P109 (activated nanoporous carbon) with BET specific surface area of 1396±24 m^2/g was used as a standard. The value of the specific surface of the experimental sample can be calculated by the formula: $S = S^{st} \cdot F^{st} \cdot m^{st}/F/m$, where S i S^{st} – is the specific surface of the sample under study and the standard, m^2/g; F i F^{st} – the area of the desorption peak of the sample and the standard (chromatographic data), arb. unit.; m i m^{st} – is the weight of the sample and the standard respectively, g. Acceptable measurement error was 10%. The gas mixture of 5 vol.% Ar (gas adsorbate) and 95 vol. % He (gas carrier) was used in the experiment.

Adsorption activity on iodine and Mass fraction of moisture were measured according to GOST 6217 [12] and GOST 12597 [13], respectively.

Table. Physico-chemical characteristics of the initial, spent and regenerated activated carbons

## AC	Sample	Specific surface area, m^2/g	Adsorption activity on iodine, %	Mass fraction of moisture, %	Mass fraction of glycerin, %
1	1initial	931	83	0,8	–
2	1spent	56	53	14,5	37.3
3	1.0 regenerated	623	64	0,6	not determined
4	1.1 regenerated	799	84	0,5	1.8
5	1.2 regenerated	542	75	0,9	6.8
6	2initial	924	92	1,3	–
7	2spent	242	48	31,3	7.1
8	2.0 regenerated	865	58	0,3	not determined
9	2.1 regenerated	447	85	0,3	not determined

Results and discussion

Figure 1 shows at the same scale the thermograms of the initial ACs (#1, #6) and spent ACs (#2, #7) activated carbons. On the thermograms of the samples, weight loss is observed with maxima at ~ 100 °C and 260 – 275 °C in the temperature range 20 – 550 °C (DTG). The first process refers to the loss of adsorbed water; it is also observed for the initial activated carbon. The second process is the evaporation of glycerin [4]. It is clearly seen from the DTG curves that H_2O is released in the temperature range 20 – 180 °C, and $C_3H_5(OH)_3$– 180 – 400 °C. This makes it possible to calculate their amount in samples (table). Spent ACs (#2/#7) contain 14,5/31,3 wt. % H_2O and 37,3/7,1 wt. % $C_3H_5(OH)_3$, respectively.

The pyrolysis reactor (Institute of Renewable Energy of the National Academy of Sciences of Ukraine, Department of Renewable Organic Energy) has been used for the regeneration of spent activated carbon (Fig. 2).

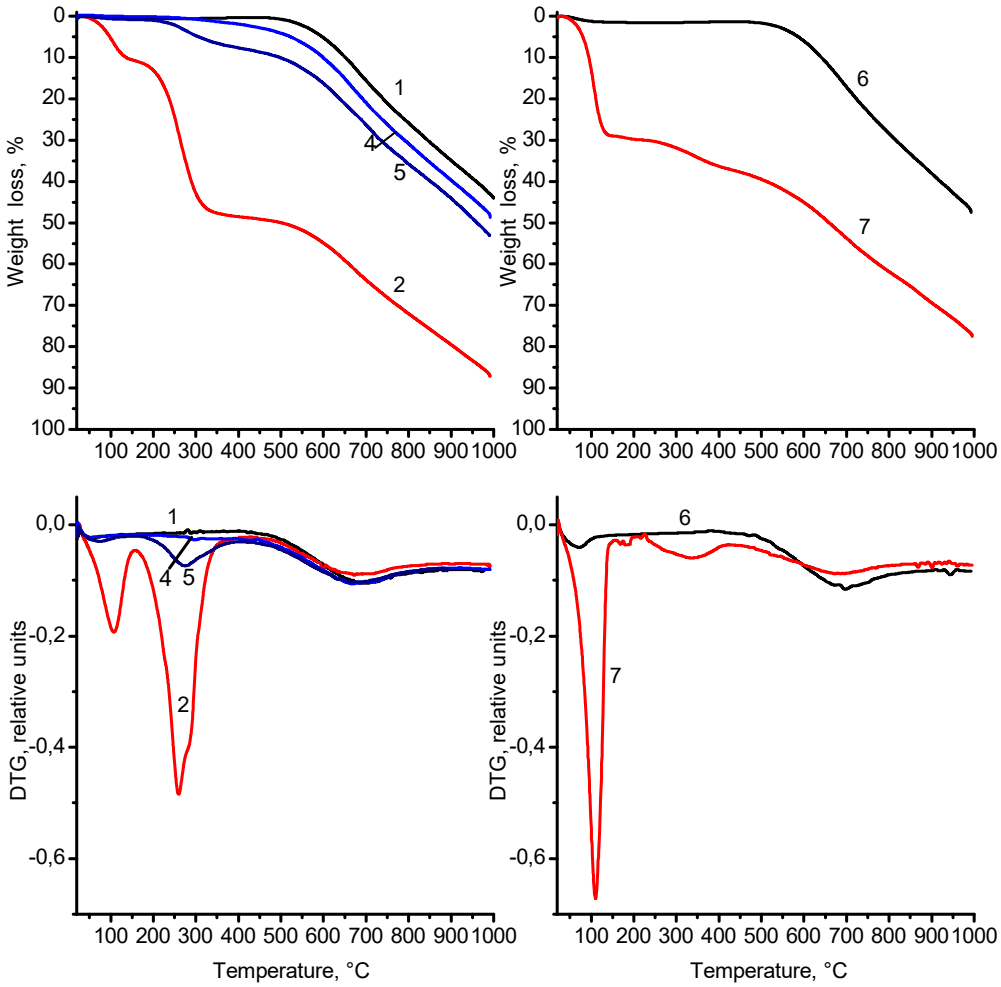

Fig. 1. TG, DTG – thermal analysis curves of initial (1, 6), spent (2, 7) and regenerated (4, 5) AC. The numbering of the curves corresponds to #AC samples as in the table

The pyrolysis reactor is designed for recycling fuel into generator gas (full gasification), or pyrolysis gas and AC (partial gasification or oxidative pyrolysis). The process of partial fuel gasification is carried out in a gas generator with a moving gasification zone (Fig. 2). After igniting the fuel (in our case, wheat straw pellets), the gasification zone begins to move towards the air flow at a constant speed. The SAC layer is continuously heated; volatile substances are released and oxidized by the blowing air. Next, the gasification reactions of SAC with water vapor and carbon dioxide formed in the pyrolysis process proceed. Behind the gasification zone remains a layer of hot AC, in which thermal decomposition of resins takes place [14].

AC2 was regenerated at three different regimes (samples 3-5) and AC7 – at two ones (samples 8, 9). The regimes differed in different rates of air supply to the lower part of the reactor.

As a result, the amount of water (Table) and glycerin in the samples were significantly reduced. The glycerin content of AC4 and AC5 was determined from TG curves (Fig. 1).

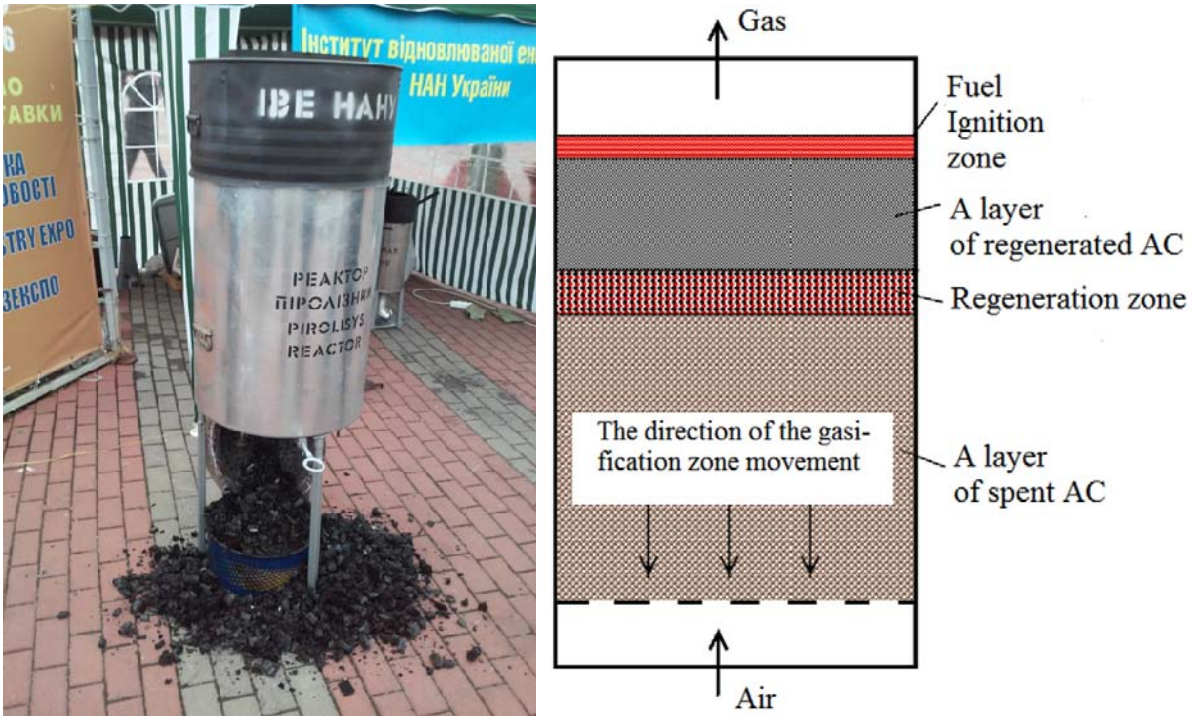

Fig. 2. Photo of the pyrolysis reactor and the scheme of regeneration of spent activated carbon

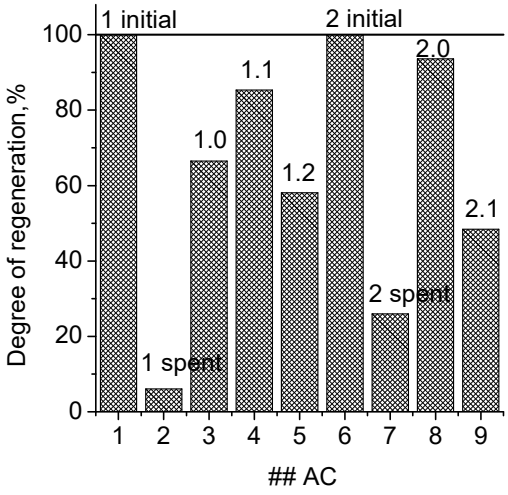

Fig. 3. The degree of AC regeneration, calculated from the values of the specific surface area

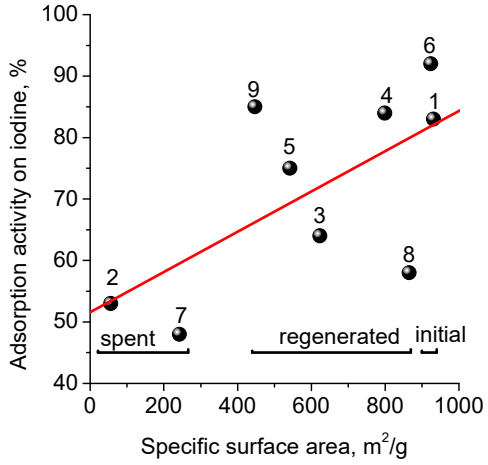

Fig. 4. Dependence between specific surface area and iodine number of ACs

The value of the specific surface area of the samples (S) was taken as a measure of the degree of regeneration. The specific surface area of the initial granular adsorbents is 931 and 924 m^2/g, respectively, and is taken as 100 %. After using these adsorbents in the process of purifying glycerin, their S decreases to 56 m^2/g (sample AC2) and to 242 m^2/g (sample AC7).

After regeneration, the specific surface area increases to 447-865 m^2/g. The highest degree of regeneration of the AC samples after activation was 85 % (AC4) and 94 % (AC8) (Fig. 3). Such ACs can be used to repurify glycerin.

The iodine number is a relative indicator of the porosity of activated carbons. The iodine number is not a measure of the ability of activated carbons to adsorb other substances. The iodine number can be used to approximate the specific surface area of some types of activated carbons. However, it must be taken into account that strict relationships between specific surface area and iodine number cannot be established. These indicators vary depending on the source material of activated carbons, on the conditions for their preparation and the pore size distribution in them. The presence of adsorbed volatile substances, sulfur and water-extractable substances in ACs can affect the value of the iodine number. [12]. As can be seen from Fig. 4, there is still a weak correlation between S and iodine number, R=0.64. Adsorption activity for iodine and S increase in the same row ACspent > ACregenerated > ACinitial. No such dependence was observed for methylene blue [4].

Conclusions

Using thermogravimetric analysis, a quantitative and qualitative evaluation of adsorbed impurities in spent activated carbon Norit 1240 after glycerol purification was carried out. It has been established that H_2O is released in the temperature range 20 – 180 °C, and $C_3H_5(OH)_3$– 180 – 400 °C. Spent AC contains up to 31.3 wt. % H_2O and up to 37.3 wt. % $C_3H_5(OH)_3$.

The pyrolysis reactor has been successfully used for the regeneration of spent activated carbon. It is shown that after the reactivation of SACs, their specific surface area is restored to 45-94 % of the initial one. There is a weak correlation between S and iodine number, R=0.64. Adsorption activity for iodine and S increase in the same row ACspent > ACregenerated > ACinitial. Subject to the optimal regeneration regime, samples suitable for reuse can be obtained.

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ПІРОЛІЗНА РЕГЕНЕРАЦІЯ АКТИВОВАНОГО ВУГІЛЛЯ ВИКОРИСТАНОГО ДЛЯ ОЧИЩЕННЯ ГЛІЦЕРИНУ

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В роботі досліджували гранульовані активовані вугілля Norit 1240 (АВ) – вихідні та відпрацьовані з адсорбованими домішками після очищення технічного гліцерину та подальшого промивання водою. Мета роботи – встановлення оптимальних умов термічної регенерації АВ на установці піролізу та кількісне визначення адсорбованих домішок у відпрацьованому АВ за допомогою термогравіметричного аналізу (ТГА). Для всіх зразків АВ вимірювали питому поверхню (S), адсорбційну активність по йоду та масову частку вологи. Методом ТГА встановлено, що вода виділяється в інтервалі температур 20 – 180 °С, а гліцерин – 180 – 400 °С. Відпрацьоване АВ містить до 31,3 мас. % H_2O і до 37,3 мас. % $C_3H_5(OH)_3$. Для регенерації зразків АВ використали піролізний реактор. Показано, що після реактивації відпрацьованих АВ їх питома поверхня відновлюється до 45-94% від початкової. Спостерігається слабка кореляція між S та йодним числом, R=0,64. Адсорбційна активність по йоду та S збільшується в тому самому ряду АВвідпрацьоване > АВрегенероване > АВвихідне. В результаті регенерації отримано активоване вугілля, придатне для повторного використання.

Ключові слова: *відпрацьоване активоване вугілля, термічний аналіз, регенерація, піролізний реактор*