

RESOURCE AND ENERGY SAVINGS IN THE PRODUCTION OF CRUDE BENZENE FROM COKE GAS**Lavrova I.***phD in technical science, Professor**National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine*<https://orcid.org/0000-0002-3970-1627><https://doi.org/10.5281/zenodo.18070657>**Abstract**

The article discusses the process of removing benzene hydrocarbons from coke gas by absorption with absorbent oils at pressures close to atmospheric pressure. It describes the physical mechanism of absorption based on mass transfer between the gas and liquid phases and the determination of equilibrium concentrations of benzene hydrocarbons according to Henry-Dalton and Raoult's laws. Diagrams of equilibrium concentrations of benzene hydrocarbons in coke oven gas and coal-based absorbent oil at different temperatures are presented, illustrating the effect of temperature and benzene concentration in oil on the efficiency of the process. The optimal operating parameters are determined, in particular, the maximum content of benzene hydrocarbons in the absorbent oil and the permissible temperature of coke oven gas to ensure high extraction efficiency. A set of measures for modernizing the installations has been proposed, including improving gas preparation, oil washing and regeneration, optimizing temperature regimes, and introducing new structural elements of the apparatus and automated control systems. A recommended technological scheme for the absorption of benzene hydrocarbons and the production of crude benzene is presented, which ensures an increase in process efficiency and a reduction in energy costs. The results of the study are of practical importance for improving coke gas purification technologies at coke chemical plants.

Keywords: process intensification, benzene hydrocarbons, coke gas, absorption, mass transfer, distillation column, hydrodynamic parameters, modernization, coal tar oil, scrubber, regular contact devices, gas purification, coke chemical production, efficiency, operating parameters, energy saving

Benzene hydrocarbons are found in coke oven gas in the form of vapors, and they can be extracted using various methods. However, absorption using absorbent oils at a pressure close to atmospheric pressure is the method most commonly used worldwide. Desorption of benzene hydrocarbons from saturated oil is carried out by blowing a large or small amount of hot steam through preheated oil.

The absorption of benzene hydrocarbons by absorbent oil is a physical process in which mutual mass transfer occurs between the gas and liquid phases in the direction of equilibrium. The state of equilibrium is determined by Henry-Dalton and Raoult's laws [1]. According to these laws, at a constant temperature, the concentration of crude benzene in the absorbent oil is proportional to the partial pressure of benzene in the gas phase. Since equilibrium concentrations are never achieved in the equipment used for the absorption process, they are usually considered as the limit towards which the process tends under specific technological conditions (temperature, pressure, quality characteristics of the absorbent oil, etc.) [2, 3].

Fig. 1 shows diagrams of equilibrium concentrations of benzene hydrocarbons in coke gas and coal tar

absorption oil at different contact temperatures. These diagrams are calculated for coal tar oil with a molecular weight of $M = 150$. According to these diagrams, if the absorbent oil supplied to the scrubbers contains only 1% of benzene hydrocarbons, the equilibrium concentration of the latter in coke oven gas will be: at 25°C – 9 g/m³; at 35°C – 12 g/m³; at 40°C – 16 g/m³. If oil containing 2 g/m³ of benzene hydrocarbons is supplied to irrigate the scrubbers, the equilibrium concentration at 40°C will be 32 g/m³. Such absorbent oil will remove practically nothing from coke gas with a normal benzene hydrocarbon content of 33 – 36 g/m³. In order to ensure that the residual content of benzene hydrocarbons in the purified gas is reduced to 3 g/m³. The Rules for Technical Operation of Coke Chemical Plants establish the following parameters:

- the absorbent oil used for extraction must contain no more than 0.3% of benzene hydrocarbons (in practice, in countries that are leaders in coke chemical production, these values are 0.1 – 0.2%);

- the average temperature of coke oven gas should not exceed 30°C (in some practice, the value of 25–28°C is more often indicated);

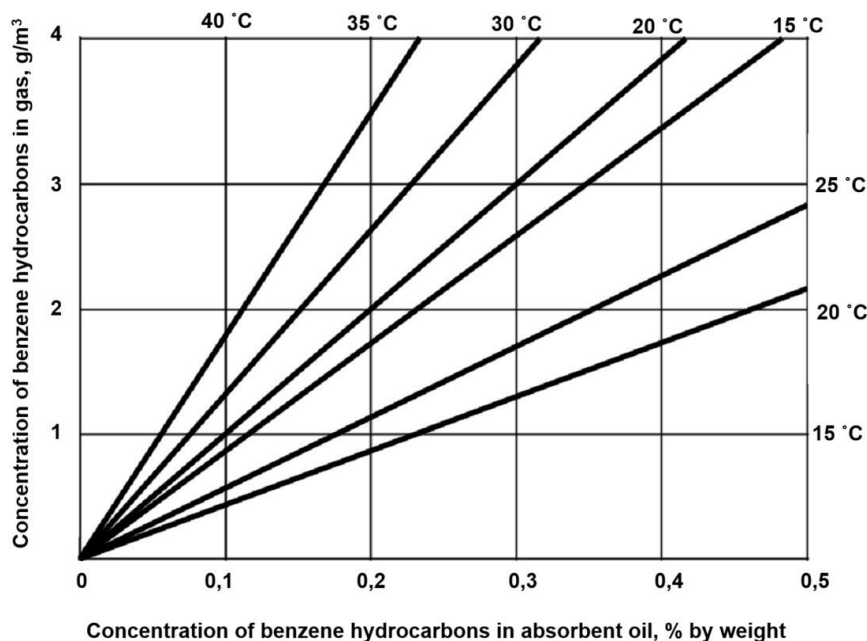


Figure 1. Diagrams of equilibrium concentrations of benzene hydrocarbons in coke gas and coal tar absorbent oil at different contact temperatures

It should be emphasized that compliance with the specified technological parameters is mandatory for all devices for the absorption of benzene hydrocarbons (regardless of the packing, injectors, plates, etc. used), as these parameters are decisive [4, 5]. The technological schemes used, equipment design, and other factors are secondary, ultimately ensuring the economics of the process.

Most coke chemical enterprises in Ukraine are characterized by increased losses of benzene hydrocarbons with reverse gas, which exceed the maximum permissible limits specified above [6]. This situation is the cumulative effect of a number of negative factors, which primarily include:

- instability of gas and absorbent oil consumption;
- unsatisfactory temperature conditions;
- low quality of recycled absorbent oil;
- unsatisfactory condition of main technological equipment;
- low availability of control and measuring devices in installations.

Many coke chemical plants are working to modernize their facilities and technological equipment and adapt them to modern technological conditions.

When modernizing existing plants and constructing new ones, the above technological parameters must be maintained and the measures and technical solutions implemented in industrial practice by advanced plants in foreign countries and Ukraine must be taken into account [7]. The main improvements include the following:

1. Better preparation of coke oven gas supplied for the removal of benzene hydrocarbons from acidic components (HCN, H_2S), naphthalene, and unsaturated compounds. One option for solving this problem is to install scrubbers for the removal of benzene hydrocarbons after desulphurization. This will significantly in-

crease the service life of coal absorption oil while increasing the depth of benzene hydrocarbon removal.

2. Washing the working absorbent oil with water to reduce its corrosive activity by washing out aggressive components. It has been established that a 60 – 70% reduction in the content of NH_4CNS , $(NH_4)_2S$, NH_4CN reduces the corrosive activity of the oil by 4 – 6 times. It is recommended to flush part of the working oil taken from circulation. Savings are achieved primarily by increasing the service life of the oil and, naturally, the service life of the main technological equipment.

3. Stabilization of the quality of working coal tar absorbent oil by regenerating part of it in order to remove the polymers formed and minimize the amount of refractory components (anthracene, carbazole, etc.) remaining in the latter.

4. Replenishment of the cycle with fresh coal absorption oil that meets the requirements of modern technical specifications for oil grade “A” or its imported analogues, which are sometimes found in the practice of coke chemical production in Ukraine.

5. Optimization of the gas and oil temperature range by differentiated supply of benzene-free absorption oil according to the stages of absorption. This technique allows reducing the content of benzene hydrocarbons in the return gas by significantly lowering the temperature of the oil supplied to the last stage of absorption without its dehydration. The essence of the proposal is to compensate for oil heat loss by adding small amounts of hot benzene-free oil to the main flow of the latter. Industrial research has shown that the proposed technological scheme allows reducing the loss of benzene hydrocarbons with the return gas by an average of 2 – 5 g/m³ compared to the traditional scheme. The temperature of the oil supplied to the last stage (along the gas flow) is reduced by an average of 7 – 8°C.

The recommended process flow diagram works as follows: coke oven gas stream I with a temperature of 25 – 28°C enters the lower part of scrubber 1, is distributed across its cross-section, and interacts on the surface of the regular packing with benzene-free absorption oil, which is distributed in the upper part and leaves the apparatus.

In turn, the saturated absorbent oil is pumped through heat exchangers 8, 10 to a tubular furnace 2, where it is heated to a temperature of 170 – 180°C. The vapors and heavy fractions of the latter are fed further to the feed plate of the stripping section of the benzene column 4. Flowing down the plates of the stripping section of the benzene column, the oil comes into contact with the rising vapor phase, which consists of water vapor, benzene hydrocarbon vapors, and absorbent oil.

As a result, the upward-moving vapor phase is enriched with volatile components, and the downward-moving liquid phase is enriched with absorbent oil components. To create an upward flow of the vapor phase in the exhausting part of the distillation column, part of the oil after the tubular furnace is fed into the upper part of the regeneration column 3, and steam III, superheated in the tubular furnace 2, is fed into the lower part of the same column. As a result, light oil fractions are distilled into distillation column 4 and the bottom residue (“polymers”) IV is subsequently removed.

Oil vapors containing benzene hydrocarbons, as well as water vapors from the exhaust section; enter the strengthening section of distillation column 4, to the top tray of which raw benzene is fed as reflux. Flowing downwards towards the oil vapor stream, the reflux evaporates completely due to the heat of the upward flow of crude benzene and water, as well as the heat of condensation of the oil vapors, which are almost completely returned to the stripping section of the column.

In turn, benzene hydrocarbon vapors are removed from the top of the strengthening section by condenser 8 and cooler 9 for complete condensation. The condensate of water vapor and benzene hydrocarbons is sent to separator 7 to separate crude benzene from water. Part of the crude benzene from the separator 7 assembly is fed by a pump as reflux to the distillation column, and the other part is removed from the cycle as a finished product (crude benzene) V.

In the strengthening part of the column, there is a certain gradient of temperature and composition of the liquid phase along the height of the column. The upper trays of the strengthening section contain mainly lower-boiling components (crude benzene) in the liquid phase. The lower trays contain mainly higher-boiling components (absorbent oil) in the liquid phase. An intermediate fraction enriched with naphthalene is selected from the middle part, separator 5. This makes it possible to actually reduce the naphthalene content in the return oil.

The main advantages of the proposed technological schemes, supported by modern technological equipment, include:

- stabilization of the quantitative composition of

the obtained crude benzene (with distillation fluctuations up to 180°C not exceeding $\pm 1\%$ in the range from 91 to 96%);

- reduction of gas pressure losses during absorption in the scrubber, which is recommended to be 30 – 50% compared to those currently used;
- reduction of steam consumption for distillation of absorbent oil by 2 – 2.5 times compared to that currently used;
- reduction in the amount of wastewater from the benzene section subject to disposal
- reduction in material and energy consumption in the development of modern absorbers with regular packing.

In recent years, there has been considerable and well-founded practical interest in scrubbers with regular packing elements, due to their high gas phase throughput capacity, large specific phase contact surface area, and low hydraulic resistance [8, 9]. That is why these devices are now used in industrial practice in coke and petrochemical production for the capture of benzene hydrocarbons, hydrogen sulfide, final cooling of coke oven gas, and others.

At the same time, the practice of operating industrial devices with regular metal packing has shown that their efficiency is often significantly lower than in tests under experimental and industrial conditions [10]. This is due to a number of reasons, the most important of which is the significantly greater complexity of the absorbent distribution than in the basic version. And even if a relatively uniform initial distribution of the absorbent is achieved, it is not always possible to maintain it throughout the height of the apparatus due to local contamination, corrosion, and technological factors affecting surface tension, wettability.

There are currently two realistic approaches to mitigating the impact of this extremely negative phenomenon, namely:

1. The most common approach, recommended by the theory of “large-scale transitions” and associated with sectioning the apparatus vertically using devices for redistributing interacting phases;
2. An approach associated with the use of packing that are capable of redistributing interacting gas (vapor) and liquid due to their design features.

The first approach has gained some popularity and is being developed through the improvement of devices for redistributing interacting phases, which have a number of complex (and sometimes contradictory) criteria, primarily including:

- even distribution of irrigation fluid across the surface of packing elements;
- minimal splashing;
- reliability in operation;
- minimal pressure loss in the distributor installation area;
- minimal energy consumption for irrigation fluid distribution;
- simplicity of devices, their manufacture, and installation;
- stable operation over a wide range of loads.

Despite the large number of different designs of these devices and the large volume of experimental and

theoretical research summarized in a series of monographs, this issue is far from being resolved.

With regard to regular packing devices, various packing-type designs have become widely used, in which the upper layer of the nozzle is completely wetted due to the fine spraying of the irrigation liquid. However, in countercurrent conditions, even in outdated “slow-speed” devices with wooden chord packing and low gas velocities, significant splash carryover was observed, which is highly undesirable.

In the operating conditions of intensive devices with regular sheet packing, where the average gas velocities are 3 – 3.5 m/s, splash carryover can reach significantly higher values. Therefore, effective splash guards must be installed to localize it [11, 12].

Coke chemical plants currently use units with regular metal packing. These are units with scrubbers with Z-shaped packing and packing distribution of absorbent oil. A characteristic feature of these scrubbers is the use of shortened flat-parallel packs as support grids under the packing and for redistributing the absorption oil. Or installations with scrubbers with flat-parallel packing, disc distribution, and intermediate redistribution of absorbent oil along the height of the apparatus. A specially designed perforated plate placed in an expansion chamber is used as a device for the primary distribution of absorbent oil, and vortex plates, similar for different scrubbers, are used as intermediate redistributors. Let us conditionally refer to these installations as option 1.

Subsequently, coke chemical plants in Ukraine began to use scrubbers with a flat-parallel packing and new disc devices for the distribution and redistribution of gas and absorbent oil [13].

Low-pressure sprayers evenly distributed in the space under the plate are used as devices for spraying the absorbent oil redistributed by the plate. To enhance the mass transfer effect, the developers envisaged mixing the absorbent oil on the plate using the energy of the gas flow (option 2). In real production conditions, with the characteristic low quality of recycled absorbent oil containing a large amount of solid inclusions, the devices quickly became clogged. In particular, with a coke oven gas consumption of about 65 thousand m³/hour and a specific consumption of coal absorption oil of 2.2 – 2.3 l/m³ of gas, the resistance of one scrubber reached values of about 4 kPa. Moreover, the main

increase in resistance occurred in the upper distribution plate and the upper tier of the packing, as well as in the lower tier of the packing and the primary gas distributor.

All of the above-mentioned benzene plants were initially designed for a gas throughput capacity of about 100000 m³/hour. All plants had the same amount of packing material placed in two sequentially connected scrubbers with a diameter of 3.6 m.

The actual performance indicators of the technical installations discussed above with different internal structural elements are shown in Table 1, which shows that technical installations with a flat-parallel packing in the first variant have higher performance and efficiency indicators for the removal of benzene hydrocarbons with acceptable pressure losses. Installations with Z-shaped packing and injector distribution of the absorber are slightly inferior in terms of extraction efficiency and total pressure losses.

Both of these options have significant advantages over the second option with a flat-parallel packing in terms of both the efficiency of benzene hydrocarbon extraction and the overall performance of the unit [14].

One of the main reasons for the lower efficiency of installations with scrubbers with Z-shaped packing is the insufficiently reliable operation of the primary oil distributors and the absence of oil redistributors along the height of the devices.

Even well-designed modern injectors in the optimal spray mode of absorbent oil have a high degree of uneven distribution across the cross-section of the apparatus.

When fluid flow fluctuates, this value increases. It is necessary to note another extremely negative fact characteristic of injector distribution of absorbent oil – increased spray carryover, which increases as the gas velocity increases. To localize it in scrubbers with a Z-shaped packing, two splash guards (louver and cyclone) are installed, made together with the shell body.

These splash guards, as will be shown below, are the main cause of increased pressure losses. When using correctly selected disc distributors, the uniformity of absorbent oil distribution is practically independent of the flow rate over a wide range of liquid loads.

Table 1.

Key performance indicators for comparable technological installations

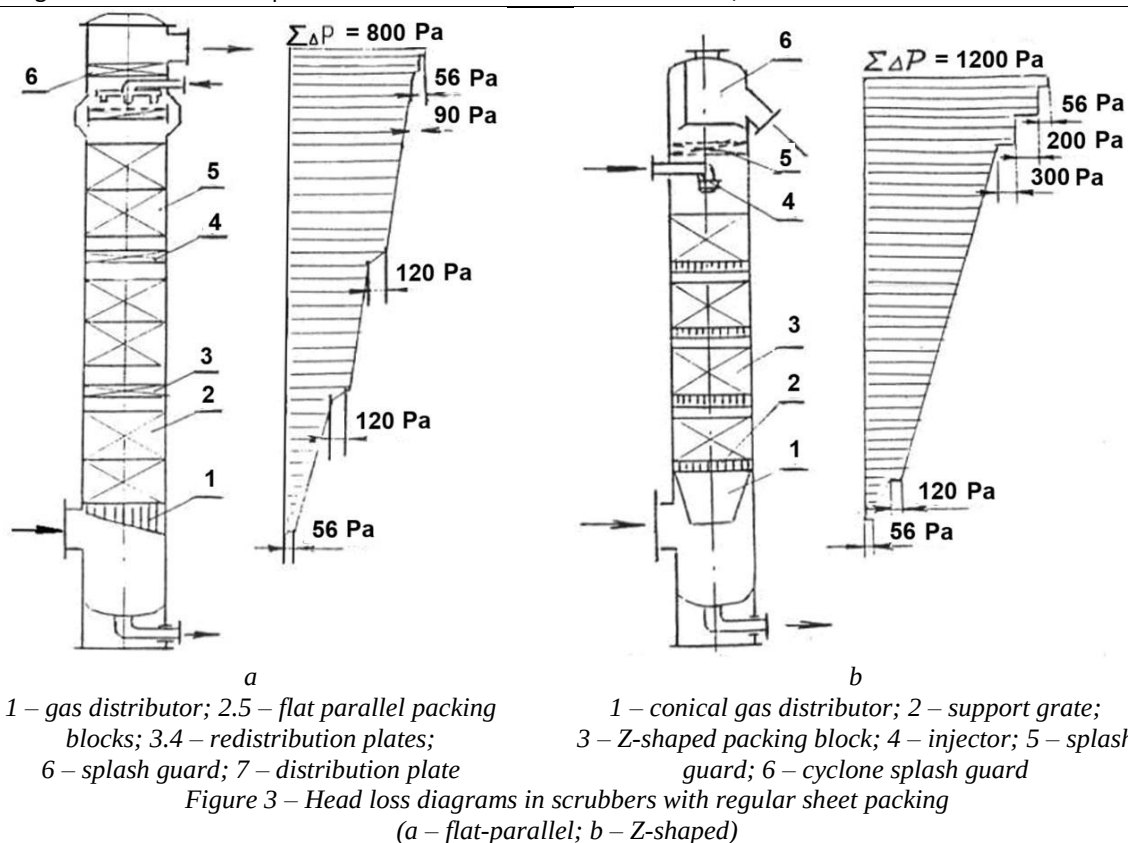
Indicators	Scrubber installations		
	with flat parallel packing		with Z-shaped packing
	option 1	option 2	
Gas throughput capacity (actual), thousand m ³ /hour	100 – 110	50 – 70	80 – 90
Consumption of coal-based absorbent oil, m ³ /hour	170 – 180	150 – 160	150 – 160
Oil temperature, °C	30	30	30
Residual content of benzene hydrocarbons in purified gas, g/m ³	3	5 – 6	4.5
Pressure loss in one scrubber, kPa	0.8 – 1	1.7 – 4*	1.2 – 1.4

* The maximum values are obtained when filling in the elements specified in the text.

When installing a disc distributor in an expansion chamber, where gas bypasses the disc along the periphery, pressure losses at the installation site are minimized.

To determine the reasons for the significant

difference in resistance between installations with a flat-parallel packing (option 1) and a Z-shaped packing, we constructed head loss diagrams calculated according to the corresponding dependencies and measured during commissioning (Fig. 3).



The data presented shows that both the overall resistance of the installations and the resistance of individual scrubbers is determined by pressure losses in auxiliary elements. Thus, for comparable scrubbers with a flat parallel packing, with a total resistance of one device of about 800 Pa, the pressure losses in the packing are only 360–380 Pa. For scrubbers with a Z-shaped packing with a total resistance of 1200 Pa, the pressure loss in the packing is only 470–490 Pa. Obviously, the use of less energy-intensive auxiliary devices will reduce the total pressure loss in the installation as a whole.

In particular, the use of a device with an expansion chamber for the primary distribution of absorbent oil in scrubbers with a Z-shaped packing will significantly reduce pressure losses (by 500–560 Pa). In turn, for scrubbers with a flat-parallel packing, it is advisable to reduce the number of redistribution devices and replace them with less energy-intensive ones. In particular, redistribution units similar to those used in scrubbers with a Z-shaped packing may be of interest as devices for redistributing absorbent oil.

Even greater opportunities for significantly reducing the energy consumption of comparable technological installations are provided by the transition to placing the required packing surface in a single device by

reducing the number of gas inlet and outlet devices. In particular, for installations with a flat-parallel packing, it is possible to reduce pressure losses by 40%, and for installations with a Z-shaped packing, by 30%.

However, it should be emphasized that the use of known packing (flat-parallel, Z-shaped) for these purposes will result in excessively tall devices ($H = 50 \text{ m}$). This, in turn, will complicate their transportation from manufacturing plants and routine maintenance (repair, painting). It is also necessary to note the increase in the cost of transporting the absorber to the top of the apparatus.

Therefore, for the practical implementation of the above-proposed areas of intensification, it is necessary to use packing elements that combine the increased throughput and low hydraulic head losses characteristic of flat-parallel and Z-shaped packing with increased efficiency.

Our research has shown that to solve the technical problem of achieving a 90–95% extraction rate of benzene hydrocarbons in a single technological apparatus, volumetric packing that eliminate a number of disadvantages inherent in various versions of flat parallel and Z-shaped packing may be of practical interest [15].

One such device is a cellular comb (honeycomb) packing (Fig. 4).

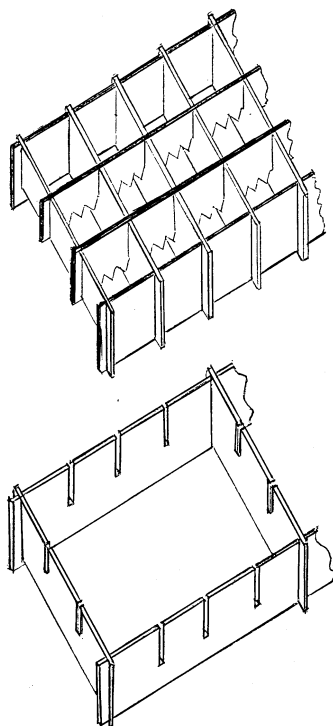


Figure 4. Element of a regular cellular comb (honeycomb) packing.

As a result of developing the cellular comb (honeycomb) packing, the range of working gas speeds has been increased to 4 – 5 m/s under conditions of low pressure loss (up to 80 – 100 Pa per 1 m of height), and it also stands out from its counterparts due to its simplicity of manufacture.

The cellular comb (honeycomb) packing has vertical square channels formed by a series of strips of sheet material installed on edge and arranged parallel to each other; they have grooves with a constant pitch on the upper edge, into which strips of sheet material are inserted. These design features allow:

1. Create a regular package that combines low metal consumption with strength.
2. Significantly simplify (and, as a result, make cheaper) the packing manufacturing process, use materials in the manufacture of the latter that cannot be used to manufacture Strepak-type packing (alloyed cast iron, some composite materials).
3. Eliminate the need for special equipment for making regular packing, which is used for cutting slots and subsequent stretching.
4. Significantly reduce the likelihood of clogging of regular packing with mechanical impurities present in technical fluids.
5. Significantly increase the turbulence of the contacting gas and liquid and the frequency of surface renewal of regular packing.

The design is explained in Fig. 4, which shows a regular cellular comb (honeycomb) packing insert consisting of strips of sheet material with grooves made at regular intervals on the upper edge of each strip, the width of which is approximately equal to the thickness of the strips. During installation, these strips are placed at regular intervals on the edge so that the grooves on each of the strips are on the same generatrix. Other strips are inserted into these grooves, which may have

saw-like drip edges at the bottom, including those spread in different directions.

Conclusions

Resource- and energy-saving technological schemes for the absorption of benzene hydrocarbons from coke gas and the production of crude benzene are based on the rational combination of an optimally selected technological regime and the use of intensive scrubbers equipped with modern high-efficiency internal structure elements (regular packing, distributors and redistributors of interacting phases).

There is a real possibility of organizing the absorption process in a single high-capacity technical apparatus, which reduces the resistance of the installation by 35 – 40% and creates the conditions for the complete automation of the process of extracting benzene hydrocarbons from coke gas.

The proposed technical solutions can be used both in the design of new benzene departments and in the reconstruction of existing enterprises.

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