



DEVELOPMENT OF A CATALYST FOR THE SYNTHESIS OF BUTADIENE-1,3 BASED ON BUTYLENES - SECONDARY PRODUCTS OF SGCC

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ABSTRACT: - Butadiene - typical diene hydrocarbon with the interfaced double communications, will easily be polymerized and copolymerizing with styrene, nitriles or air of acrylic or methacrylic acids, blamed - and methylvinylpyridine, blamed - and vinylidene chloride, isobutylene, an isoprene, etc. Butadiene is the main monomer applied in modern industrial production of synthetic rubbers. One of decisive factors at determination of prospects of this or that method of synthesis of butadiene is existence of resources and cost of used raw materials. The method of two-phasic dehydrogenation of butadiene, despite simplicity of the basis of chemical transformations, demands creation of very difficult and powerintensive technology. It induced many researchers to search of conditions of reaction of dehydrogenation of butadiene under which the exit of butadiene would be maximum. Process of vacuum dehydrogenation of butadiene is developed in the USA by Gudri's firm.

“DEVELOPMENT OF A CATALYST FOR THE SYNTHESIS OF BUTADIENE-1,3 BASED ON BUTYLENES - SECONDARY PRODUCTS OF SGCC”

KEYWORDS: Dehydrogenation, butadiene, butane, butylene, Gudri method.

INTRODUCTION

Butadiene - 1,3 (divinyl) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ is a colorless gas with a characteristic unpleasant odor and a boiling point of 268.59 K. Butadiene is the main monomer used in the modern industrial production of synthetic rubbers. The production of the vast majority of general-purpose synthetic rubbers is based on butadiene: stereoregular 1,4-cisbutadiene, styrene-butadiene, methylstyrene-butadiene, a number of special-purpose synthetic rubbers - nitrile butadiene, butadiene-methylvinylpyridine, etc. In addition to the production of synthetic rubbers, butadiene is used on an industrial scale for the production of synthetic resins, adiponitrile (in the production of polyamides) and sebacic acid. For the first time, the process of obtaining butadiene from ethyl alcohol was developed by S.V. Lebedev (USSR). Subsequently it was developed in the USA. The process for the production of butadiene by the reaction of acetylene with formaldehyde (the Reppe process) was first implemented in Germany. Then they developed processes for obtaining butadiene through aldol condensation of acetaldehyde (Germany) and dehydration and dehydrogenation of ethanol (Soviet Union, USA). Currently, butadiene is obtained from petroleum feedstocks by separation from the C4 fraction of steam cracking and dehydrogenation of butane and partially butene, also contained in the C4 fraction of steam cracking. Industrial methods for producing butadiene from butane or butene-1.

The production of butadiene from C4 hydrocarbons (n-butane and n-butenes) by catalytic dehydrogenation is the main direction in modern butadiene production technology. In industry, various technological

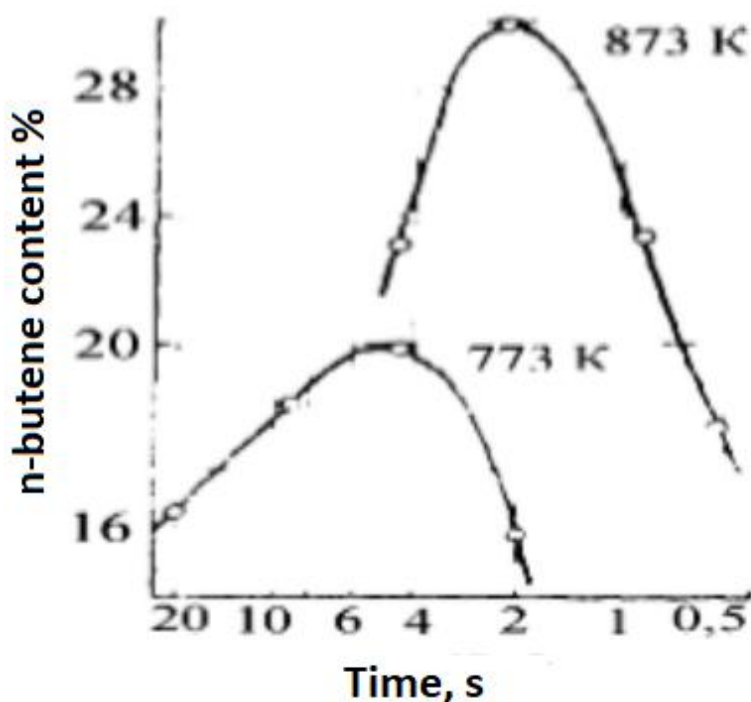
options for the production of butadiene by the dehydrogenation of C4 hydrocarbons are used. The applied processes can be conditionally divided into the following groups: dehydrogenation of butane into butenes, dehydrogenation of butenes; one-stage and two-stage dehydrogenation of butane to butadiene. A characteristic feature of dehydrogenation reactions with the formation of olefins is the restriction of the degree of conversion by equilibrium conditions. Dehydrogenation reactions are always endothermic and therefore the equilibrium towards the formation of unsaturated hydrocarbons must shift with increasing temperature. The degree of hydrocarbon conversion increases with increasing temperature and decreasing pressure. In practice, at temperatures above 773-823K, even in the absence of catalysts, saturated hydrocarbons undergo isomerization, cracking, etc. Therefore, the process of butane dehydrogenation is carried out at temperatures up to 923-973K, i.e. at temperatures lower than the thermodynamic optimum. The use of catalysts makes it possible to achieve a high rate of the process at a relatively low temperature, when the contribution of side reactions is not yet significant. Due to the reversibility of dehydrogenation reactions - hydrogenation and, therefore, the ability of catalysts to accelerate reversible reactions in both directions, these reactions are catalyzed by the same compounds. During dehydrogenation, due to the removal of hydrogen, an increase in the volume of gas always occurs, and a decrease in pressure favors an increase in the degree of conversion. For this reason, dehydrogenation

“DEVELOPMENT OF A CATALYST FOR THE SYNTHESIS OF BUTADIENE-1,3 BASED ON BUTYLENES - SECONDARY PRODUCTS OF SGCC”

processes are carried out at a pressure close to atmospheric, and in some cases the process is carried out in a vacuum. Sometimes, instead of using a vacuum, it is preferable to dilute the reaction mass with a gas that is inert under the reaction conditions, or with steam, which also leads to a decrease in the partial pressures of the reagents and an increase in the equilibrium degree of conversion. Lowering the partial

pressure also makes it possible to lower the reaction temperature and, consequently, to reduce the formation of by-products. An important parameter in the dehydrogenation reaction is contact time reactionary

catalyst mixtures. Pic. 1 illustrates the effect of temperature and reaction time on butene content.



Pic. 1 - Dependence of the content of n-butenes in the catalytic dehydrogenation of n-butane on temperature and reaction time.

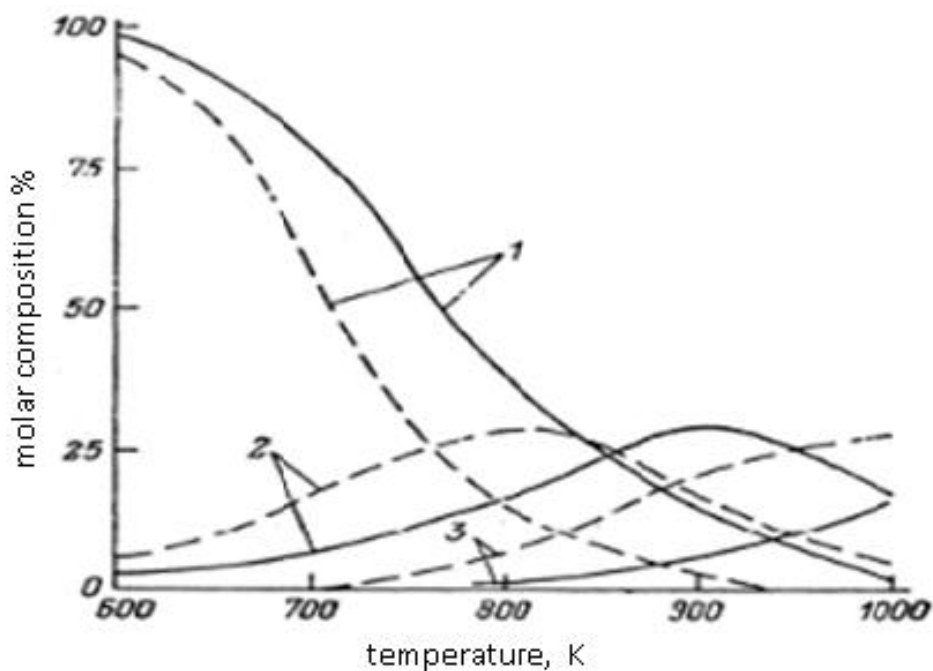
The maximum yield of olefins does not correspond to the calculated equilibrium concentration at the corresponding temperature: it is always much lower. With an increase in reaction time above the optimum, the yield of olefins decreases, since the contribution of side reactions increases. Work on the catalytic dehydrogenation of n-butane in a two-stage version: n-butane → n-butene → butadiene was started in the USA in the 1920s. In the Soviet Union, fundamental research in this area was carried out by S.V. Lebedev, N.I. Shuikin, A.A. Balandin, B.A. Kazansky and others.

One-step dehydrogenation of butane to butadiene One-step process for dehydrogenation of alkanes:



has obvious advantages over a two-stage process due to the absence of the need to separate gas mixtures after each stage and lower energy and capital costs. Pic 2 shows the dependence of the composition of the equilibrium mixture during the dehydrogenation of butane into butenes and butadiene on temperature and pressure.

“DEVELOPMENT OF A CATALYST FOR THE SYNTHESIS OF BUTADIENE-1,3 BASED ON BUTYLENES - SECONDARY PRODUCTS OF SGCC”

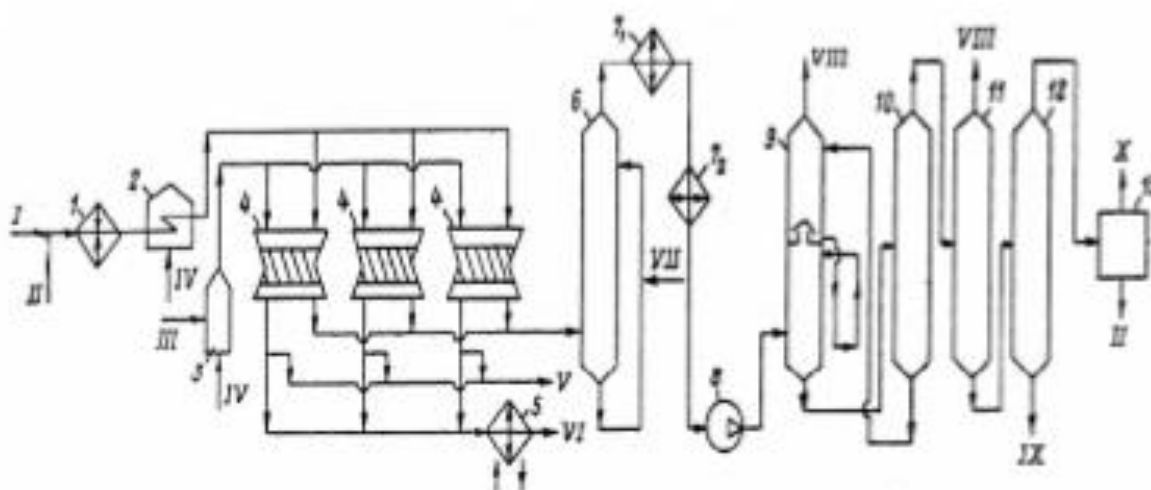


Pic. 2 - Dependence of the composition of the equilibrium mixture during the dehydrogenation of butane to butenes and butadiene on temperature and pressure. Solid lines - 0.1 MPa, dashed lines - 0.01 MPa. 1 - butane; 2 - butenes; 3 - butadiene.

Thermodynamic calculations show that the equilibrium yield of the diene increases significantly with an increase in temperature and with a decrease in the partial pressure of the alkane. Since an increase in temperature is associated with a loss of reaction selectivity, one-stage production of dienes from alkanes was carried out under vacuum dehydrogenation conditions. In a single-stage dehydrogenation process, aluminum-chromium catalysts containing 18-30% chromium oxide are used. Goodry (USA) was the first company to implement the process of obtaining butadiene from butane in one stage (similar to the process of obtaining isoprene from isopentane). In the presence of an aluminum-chromium catalyst, side transformations of butane, butenes, and butadiene occur. The use of an aluminum-chromium catalyst eliminates the use of steam as a diluent. A schematic flow diagram of this process, which is carried out under vacuum (0.015-0.020 MPa) in a stationary catalyst bed, is shown in Fig. 3. The raw

material - a mixture of butane and a return butane-butane fraction - evaporates in evaporator 1 and enters tube furnace 2 at 313 K. Superheated vapors raw materials at a speed of 240 are sent to the reactor 4, where at 863-898K and a residual pressure of 11.3-22.7 kPa is the process of dehydrogenation. The reactor is a horizontal cylindrical apparatus with a diameter of 6 m and a length of 12 m. A full working cycle lasts 21 minutes. 30s., dehydrogenation - 8 min. 15s. steam purge, reactor emptying - 2 min. 35s. From the reactor block, the contact gas is fed into a scrubber 6 irrigated with cooling oil, in which it is cooled to 328K, and then into a butadiene recovery unit. The conversion of butane in a one-stage process is ~ 20%, and the yield of butadiene is 50-55% for the converted raw material. The contact gas contains 37-39% butane, 23-25% butenes, 12-13% butadiene. The main parameters of the processes of dehydrogenation of C4-C5 alkenes are given in table one.

“DEVELOPMENT OF A CATALYST FOR THE SYNTHESIS OF BUTADIENE-1,3 BASED ON BUTYLENES - SECONDARY PRODUCTS OF SGCC”



Pic. 3. Schematic diagram of the process of one-stage dehydrogenation of butane 1 - evaporator; 2 - tubular furnace; 3 - firebox; 4 - reactors; 5 - waste heat boiler; 6 - scrubber; 7 - refrigerator; 8 - turbocharger; 9 - absorber; 10 - desorber; 11, 12 - distillation columns; 13 - extractive distillation unit. Flows: I - fresh butane; II - return butane-butylene fraction; III - air; IV - fuel gas; V - vacuum line; VI - discharge into the atmosphere; VII - blowing into the fuel network; VIII - C3 hydrocarbons for combustion; IX - fraction C4-C12; X is butadiene.

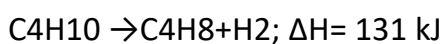
Table 1:
Parameters of process of one-stage dehydrogenation of butane

Options	Butene fraction
Reactor temperature, K	873-923
Feed volume rate, ч^{-1}	130-180
Molar ratio of alkenes : water vapor	1:20
Catalyst regeneration temperature, K	873-923

Pressure drop along the catalyst bed, MPa	0.05-0.09
Feedstock conversion rate, %	40
Diene selectivity, %	85
Diene yield based on raw materials passed, %	33
Content in contact gas, % Alkenes	59
Dienes	24

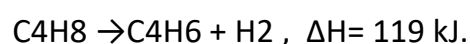
Two step process

Most industrial installations for the production of divinyl from butane operate in a two-stage scheme. The first stage of dehydrogenation of butane is to convert it to butylene, and the second is the process of obtaining divinyl from butylene, the dehydrogenation of butane to butylene on a chromium oxide promoted catalyst supported on alumina proceeds according to the reaction:



Side reactions also take place in industrial reactors: the reverse reaction of butylene hydrogenation, cracking of butane and butylene, isomerization of butane and butylene, and carbon formation reactions. At Soviet industrial installations for butane dehydrogenation, systems with a fluidized bed of a fine-grained aluminum-chromium catalyst of grade K-5 are used. In the process of butane dehydrogenation, the catalyst is covered with carbon deposits and changes its chemical composition. In this case, the activity of the catalyst sharply decreases. For the purpose of reactivation, the catalyst is continuously withdrawn from the reactor and calcined in a stream of air in a fluidized bed regenerator. In this case, carbonaceous compounds burn out, and lower chromium

oxides are oxidized to Cr_2O_3 . The dehydrogenation of butylene to divinyl proceeds on a chromium-calcium-phosphate catalyst according to the reaction:



Butadiene decomposes at elevated temperatures; therefore, in order to maintain a sufficiently high butadiene selectivity, in practice it is necessary to resort to lowering the partial pressure of the reaction gases by using superheated water vapor or vacuum. The optimum temperature of the feedstock at the inlet to the reactor is 860-910K. The two-stage process makes it possible to create optimal conditions for its flow at each stage, ensuring the maximum yield of products and selectivity. Fluidized bed apparatuses are widely used for the first stage. Such devices have a number of advantages in comparison with devices in which the catalyst is fixedly located on several plates: 1) isothermal layer, which is achieved due to active mixing; 2) fluidity of the bed, as a result of which it becomes possible to transport the coked catalyst from the reactor to the regenerator and back; 3) high surface of interfacial exchange, due to the small particle size of the catalyst, resulting in a high rate of heat transfer and mass transfer; 4) low hydraulic resistance of the layer, providing a reduction

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in energy costs and increasing the speed of the process.

Thus, in the design of the CS reactor, all the regularities of carrying out heterogeneous catalytic reactions are observed. The processes of dehydrogenation and regeneration are carried out in different devices of the same design. Unlike the first, the second stage takes place in adiabatic reactors with a fixed catalyst bed. The heat required for the reaction is supplied with superheated steam mixed with the feedstock. The advantage of these devices is the simplicity of design, the disadvantages are uneven temperature distribution in the bed, high hydraulic resistance of the device, deterioration in the efficiency of the reactor as the catalyst is coking, the frequency of operation of the device, alternately operating in the dehydrogenation mode, then in the regeneration mode. The stage is carried out at a higher temperature and reduced partial pressure, which is achieved by diluting the butenes with water vapor.

The temperature for different types of catalyst ranges from 580 to 677, diluted with steam in a ratio of 20:1. Contact gas cooling (quenching) is carried out by injection of water condensate, further cooling of the gas takes place in the waste heat boiler, then the gas is sent to the scrubber for washing and further to separation. The output of butadiene from the mass of the original butene is 20-35%. Selectivity ranges from 73 to 94%. The advantages of a one-stage process of dehydrogenation of n-butane to butadiene-1,3 are: a significant reduction in consumption process steam; the use of the heat of catalyst regeneration and the dehydrogenation reaction in the adiabatic mode and, as a result, the simplicity of the design of the reactor and the absence of complex heat exchange equipment;

elimination of the second stage of dehydrogenation and separation operations butane butylene fraction. Due to this relatively the low yield of butadiene-1,3 (12-14%) and the degree of conversion of n-butane (not exceeding 0.2) are offset by lower capital costs and energy intensity of production and, as a result, lower cost of butadiene-1 than in the two-stage method ,3.

Accordingly, after analyzing the above, it can be seen that the method of two-stage dehydrogenation of butane energy-intensive and requires a complex technological scheme. For industrial implementation, this is unprofitable, since significant energy costs will be required. Therefore, there was a need to find an alternative method of dehydrogenation. It turned out that this process can also be carried out according to a single-stage scheme, although the thermodynamics of the process sets a clear limit for the yield of the target product. But with an increase in temperature and a decrease in pressure, good results can be achieved according to this scheme. In this article, as a solution to the problem, the method of dehydrogenation under vacuum, invented in the USA by the Goodry company, is considered. As it turned out, this method has a number of advantages and gives a good yield of the product. To increase the yield of target products, increase selectivity and reduce material costs, it is necessary to conduct further studies of the effect of vacuum depth on the dehydrogenation of butanes and butylenes.

REFERENCES

1. Averko-Antonovich L.A. Chemistry and technology of synthetic rubber. - M.: Chemistry, Kolos, 2008. - 357 p.
2. Zhuravleva K.A. Obtaining styrene by dehydrogenation of ethylbenzene / K.A. Zhuravleva, A.A. Nazarov //

“DEVELOPMENT OF A CATALYST FOR THE SYNTHESIS OF BUTADIENE-1,3 BASED ON BUTYLENES - SECONDARY PRODUCTS OF SGCC”

- Bulletin of the Kazan Technological University. - 2012. - V. 15 No. 12. - p. 149-152.
3. Kozienco A.I. Fundamentals of petrochemical synthesis: textbook. allowance / A. I. Kozienco, T. A., Podgorbunskaya, D. V. Gendin. - Irkutsk: Publishing House of ISTU, 2007. - 60 p.
 4. Osipov E.V. Reconstruction of vacuum-creating systems of the department for processing waste products from the production of phenolacetone / E.V. Osipov, S.I. Ponikarov, E.Sh. Telyakov, K.S. Sadykov // Bulletin of the Kazan Technological University. No. 18. – 2011.- p. 47-52.
 5. Timofeev V.S. Principles of technology of basic organic and petrochemical synthesis: Textbook for universities / V.S. Timofeev, L.A. Seraphim. - 2nd ed., revised. - M .: Higher. school, 2003. - 536 p.
 6. Khakimullin R.R. Obtaining isoprene by dehydrogenation of isopentane and isoamylene / R.R. Khakimullin, A.A. Nazarov, S.A. Vilokhin // Bulletin of the Kazan Technological University. - 2012. - V. 15 No. 16. - p. 154-156.