

ПОЛУЧЕНИЕ СТИРОЛА ПОСЛЕДОВАТЕЛЬНЫМ СИНТЕЗОМ И ДЕГИДРИРОВАНИЕМ ЦИКЛОДИМЕРОВ БУТАДИЕНА-1,3

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В работе представлены результаты экспериментальных исследований двухстадийного процесса получения стирола из бутадиена-1,3 путем последовательного синтеза циклодимеров бутадиена-1,3 (4-винилциклогексена-1 и циклооктадиена-1,4) на первой стадии и стирола на второй стадии. Целью исследований явились увеличение производительности процесса, повышение его селективности и упрощение технологии получения стирола и этилбензола из одного вида сырья — н-бутана. Показана возможность получения 4-винилциклогексена-1 и циклооктадиена-1,4 термической и каталитической димеризацией бутадиена-1,3 на установках периодического действия с применением в качестве катализаторов нитрата меди, комплексной соли меди $[Cu(NH_3)_4](NO_2)$, пентакарбонила железа, трихлорида железа. Установлены закономерности процесса термической димеризации бутадиена в газовой фазе на установке непрерывного действия. Поставленная цель достигнута проведением синтеза димеров бутадиена на проточной установке в газовой фазе при повышенной температуре и невысоком давлении, в присутствии водяного пара и ингибитора смолообразования. Приведены результаты лабораторных исследований процесса получения стирола дегидрированием 4-винилциклогексена-1 в присутствии промышленных катализаторов дегидрирования углеводородов: палладиевого 1,0% Pd/ γ -Al₂O₃ (АП), платинового 0,6% Pt/ γ -Al₂O₃ (ИП-62), окисного железо-хром-калиевого (К-28) алюмохромового гранулированного для одностадийного дегидрирования н-бутана фирмы «Houdry». Установлена возможность получения стирола дегидрированием 4-винилциклогексена-1 на промышленном катализаторе дегидрирования этилбензола. Показано, что превращение 4-винилциклогексена-1 в стирол протекает при повышении температуры выше 400 °С через стадию образования этилбензола. При дегидрировании 4-винилциклогексена-1 выявлена избирательность по этилбензолу на алюмохромовом катализаторе дегидрирования парафиновых углеводородов состава 18-20%Cr₂O₃, γ Al₂O₃. По полученным результатам выбраны оптимальные условия проведения процесса.

Ключевые слова: 4-винилциклогексен-1, циклооктадиен-1,4, бутадиен-1,3, стирол, димеризация, дегидрирование, катализатор, установка, реактор, параметры процесса, выход, селективность, конверсия

STYRENE PRODUCTION BY SEQUENTIAL SYNTHESIS AND BUTADIENE-1,3 CYCLODIMERS DEHYDROGENATION

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The paper presents the results of the experimental research of a two-stage process for styrene production from butadiene-1,3 by a sequential synthesis of the butadiene-1,3 (4-vinylcyclohexene-1 and cyclooctadiene) cyclodimers in the first stage and styrene – in the second stage. The

purpose of the research is to increase the productivity of the process and its selectivity and to simplify the technology for producing styrene and ethylbenzene from one type of raw material – n-butane. The possibility of producing 4-vinylcyclohexene-1 and cyclooctadiene by thermal and catalytic butadiene-1,3 dimerization on batch and continuous installations using copper nitrate, copper $[Cu(NH_3)_4](NO_2)$ complex salt, iron pentacarbonyl, iron trichloride as catalysts is shown, as well as the regularities of the thermal butadiene dimerization process in the gas phase are established. The goal has been achieved by carrying out the synthesis of butadiene dimers on a flow-through installation in the gas phase at a high temperature and low pressure, in the presence of water vapor and a gum inhibitor. The results of laboratory research of the process for the styrene production by 4-vinylcyclohexene-1 dehydrogenation at the industrial catalysts for the hydrocarbons dehydrogenation: palladium 1.0% $Pd/\gamma-Al_2O_3$ (AP), platinum 0.6% $Pt/\gamma-Al_2O_3$ (IP-62), iron-chromium-potassium oxide (K-28) aluminum-chromium granulated for one-step dehydrogenation of n-butane produced by "Houdry" are presented. The possibility of styrene production by 4-vinylcyclohexene-1 dehydrogenation at the industrial catalyst for the ethylbenzene dehydrogenation has been established. It is shown that turning 4-vinylcyclohexene-1 into styrene occurs with an increase in temperature above 400 °C through the ethylbenzene-forming stage. When dehydrating 4-vinylcyclohexene-1, selectivity for ethylbenzene on the aluminum-chromium catalyst for the dehydrogenation of paraffin hydrocarbons with the composition of 18–20% Cr_2O_3 , $\gamma-Al_2O_3$ has been revealed. According to the results obtained, optimal conditions for the process have been chosen.

Key words: 4-vinylcyclohexene-1, cyclooctadiene, butadiene-1,3, styrene, dimerization, dehydrogenation, catalyst, installation, reactor, process parameters, yield, selectivity, conversion

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INTRODUCTION

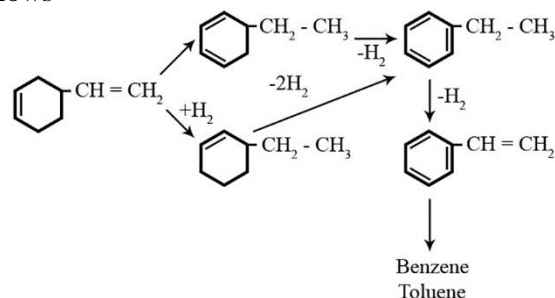
In terms of production volumes, styrene-butadiene rubbers, oligomers and other products take one of the first places in the world. Styrene (vinyl benzene, phenyl ethylene) $C_6H_5-CH=CH_2$ – one of the most important monomers – is used in the synthetic rubber industry to produce styrene butadiene rubbers and latexes, polystyrene and copolymers of styrene in the plastics industry, as well as paint and varnish, chemical pharmaceutical and other industries. The production of the initial monomers – butadiene and styrene – is based on different raw materials and different technologies; therefore, to produce butadiene-styrene copolymers, it is necessary to have two monomer productions: butadiene and styrene. It is more efficient and more profitable to use one source hydrocarbon, n-butane, and produce styrene along a single technological chain. Butadiene-1,3 and styrene are strategically important, but scarce monomers for the Russian Federation [1-4].

The 4-vinylcyclohexene-1 production by butadiene dimerization has been studied theoretically and experimentally quite well [5-7], but has found no practical application due to the lack of industrial technology. The studied butadiene cycloolimer production methods are thermal processes with inhibitors and cat-

alytic processes [8], while both of them have their positive and negative sides.

The high-yield vinylcyclohexene (VCH) is dehydrated to styrene on an iron-chromium-potassium oxide catalyst used in industry to dehydrogenate ethylbenzene. To improve significantly the use of the energy potential of the process in industrial production is possible through the use of catalysts with high activity and selectivity at lower temperatures [9-11].

The general scheme of conversion of VCH on an oxide iron-chromium catalyst can be represented as follows



One of the latest developments is a new two-stage process by the company *Dow Chemical* (USA) for the production of styrene from the C₄ fraction, a by-product of the pyrolysis ethylene production. The process involves the cyclodimerization of butadiene-1,3 to

VCH, followed by its oxidation to styrene. Cyclodimerization is carried out in the liquid phase in the presence of copper on zeolite as a catalyst, which has a high selectivity with respect to butadiene-1,3 (more than 99%). In the second stage, the VCH is oxidized with oxygen in the presence of water vapor. Conversion exceeds 90%, the selectivity of the conversion of VCH to styrene – 92%, and ethylbenzene – 2%. The process has been tested on a pilot plant with a raw material capacity of 18 kg/h. The cost of styrene production by the new process is 13-22 cent/kg lower than by traditional synthesis and ethylbenzene dehydrogenation [12].

RESEARCH PROCEDURE

The 1,3-butadiene cyclodimer synthesis has been carried out on a batch laboratory installation under the following conditions: temperature – 175 °C; time – 4 h; pressure in the reactor – 1.5-1.6 MPa [13-15].

Butadiene-1,3 was used as a raw material with the content of the main substance of 99.3% by weight. Hydroquinone, tert-butyl pyrocatechin (TBP), hydrazine were used as a polymerization inhibitor. The inhibitor was added in the calculation of 1-3% by weight on raw materials and solvent. The following were used as the solvent: *o*-xylene, diesel fuel fraction 210-250 °C, *n*-decane, concentrated diethyl benzene fraction (the content of isomers of diethyl benzene is 98.72% by weight). Copper nitrate, complex copper salt [Cu(NH₃)₄](NO₂), iron pentacarbonyl, and iron trichloride were used as catalysts.

For comparison, syntheses have been carried out on a laboratory flow-through installation. Synthesis conditions are: reactor temperature – 350-400 °C, evaporator temperature – 175-200 °C, pressure in the reactor – 0.5-1.6 MPa.

Since during the experiment the coke is deposited on the inner surface of the reactor, it is necessary to clean periodically the reactor for 8-16 h with air at 450 °C and to control the carbon dioxide content at the reactor outlet.

The second stage in the research was to study the process of 1,3-butadiene cyclodimers dehydrogenation to styrene. VCH with the content of the main substance 84-92% by weight and a small amount of another dimer – cyclooctadiene-1,4 (COD) up to 5% by weight have been used as the raw material.

The following catalysts were used: palladium 1.0% Pd/ γ -Al₂O₃ (AP), platinum 0.6% Pt/ γ -Al₂O₃ (IP-62), oxide iron-chromium-potassium (K-28), granulated aluminum chromium for one-step dehydrogenation of *n*-butane produced by the company *Houdry*. The synthesis of styrene has been studied on a flow-through installation under the following conditions [16-18]. The conditions for styrene synthesis are represented in table.

Table

The conditions for styrene synthesis
Таблица. Условия синтеза стирола

Parameters	Catalyst			
	AP	IP-62	K-28	company «Houdry»
T _{evaporator} , °C	150	150	150	200
T _{reactor} , °C	150-450	200-400	400-600	500-550
v _{raw material supply} , g/g _{cat} ·h	1.0-1.5	1.1-2.7	0.15-0.45	0.3-0.4
Y _{air supply} , l/min	1-1.8	0.8-1.2	—	—
VCH:H ₂ O, mole	—	—	1:12	—
T _{experiment} , h	1.0	1.0	1.0	0.5
τ _{regeneration} , h	1.0	1.0	1.0	1.0

The catalyst has been regenerated for 1 hour in a stream of air at the temperature of 50 °C higher than the reaction temperature, and the content of carbon dioxide in the air at the reactor outlet has been analyzed.

The analysis of raw materials, dimerizate, styrene synthesis products have been carried out by gas chromatography using specialized software [16-18]. The raw material analysis has been made on the device "Crystal-lux" with ionization-flame detector, as well the analysis of dimerizate and styrene synthesis products – on the device "Cvet-500M" with a thermal conductivity detector. The air analysis for carbon dioxide content has been carried out on the LHM-80 device with a thermal conductivity detector.

RESULTS AND DISCUSSION

On the batch installation in the reactor with a stirrer, fairly stable results are obtained. With a total partial pressure of butadiene of 1.5-1.6 MPa and the temperature of 150-280 °C, it is possible to achieve a conversion of butadiene (α) to more than 90% by weight when the selectivity for cyclodimers (VCH + COD) ($\beta_{VCH + COD}$) is higher than 70% by weight. The yield of by-products of oligomers (β_{olig}) is 28.45% by weight [13].

Some regularities of the process have been established: the presence and type of solvent influence the dimerization process, namely: in the absence of a solvent, the process goes weakly with low conversion of butadiene. In the presence of solvents based on aromatic hydrocarbons, the process is quite intensive. The optimal solvent is *o*-xylene or a mixture of xylenes, and also a mixture of diethylbenzenes [17]. In their presence, the conversion of butadiene at 175-280 °C reaches 80-90% by weight, with selectivity to the target products of 85-95% by weight.

It is possible to conduct selective dimerization in the presence of solvents based on aliphatic hydrocarbons: diesel fuel fraction, *n*-decane. However, in this case, the conversion of butadiene is less than 50% by weight at the temperatures up to 160 °C, and at the temperatures above 200 °C there is an increase in the formation of polymers.

The most effective polymerization inhibitors are *tert*-butyl pyrocatechin (TBC) and hydrazine in an amount of 1-3% by weight on raw materials.

The catalytic dimerization of butadiene has been studied in homogeneous catalytic systems: $\text{Cu}(\text{NO}_3)_2$, FeCl_3 , $[\text{Cu}(\text{NH}_3)_4](\text{NO}_2)$, $\text{Fe}(\text{CO})_5$. A polymerization inhibitor hydroquinone or TBC has been also added to the system in a mass ratio to the catalyst ≤ 1 . The results are presented in the papers [13-15]. It is found that in the temperature range of 150-220 °C, no acceleration of the reaction is observed. The maximum yield of the target products at the low temperatures of 90-100 °C is achieved in the presence of $\text{Fe}(\text{CO})_5$ at the level of 96-98% mass.

It has been established that in the experiments carried out according to the described methods [6] on the heterogeneous copper-containing catalysts the resinification of the catalysts occurs, which leads to a rapid loss of their activity to zero. Regeneration does not restore their activity; therefore, the use of heterogeneous catalysts using this technology is inefficient.

The most effective experiments on the VCH synthesis on a flow-through installation in water vapor containing hydrazine under a slight excess pressure in the reactor were carried out. Under these conditions, much less oligomers are formed and the selectivity of the formation of butadiene dimers increases.

Conversion of butadiene per cycle is up to 66% by weight with a selectivity of 70-98% by weight, the yield of side oligomers is from 10 to 25% by weight. The yield of side oligomers is strongly influenced by the temperature and partial pressure of butadiene. The optimal process parameters will be: a temperature of 220-300 °C and a pressure of 0.1-0.5 MPa. The reaction time affects both the conversion of butadiene into the target products and the yield of polymers. The optimal contact time of butadiene in the reactor is 0.5-1.5 h, depending on the temperature.

The results of experiments on the VCH dehydrogenation on three different types of catalysts are presented below. The first type includes the AP catalyst (palladium on a carrier $\gamma\text{-Al}_2\text{O}_3$) and the IP-62 catalyst (platinum on a carrier $\gamma\text{-Al}_2\text{O}_3$), which are catalysts for the process of aromatization of paraffinic hydrocarbons. Oxidative dehydrogenation is carried out in the presence of oxygen at temperatures below 400 °C.

With an increase in temperature, the yield of ethylbenzene is gradually decreased, and, accordingly, the yield of styrene is increased (Fig. 1). The maximum conversion of VCH and COD butadiene dimers in the experiments has been observed on the AP catalyst at the temperature of 300 to 400 °C and was more than 42%. The use of the IP-62 catalyst does not give satisfactory results (conversion $\sim 16\%$) [16]. At higher temperatures, the surface of the catalyst granules is coked with resinated products and decomposition products, and coke burn-off is required.

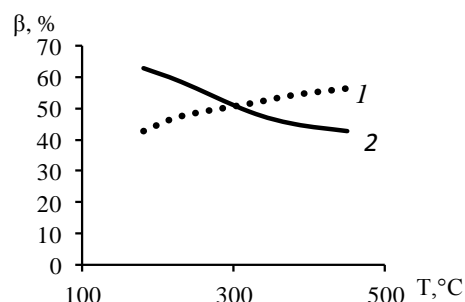


Fig. 1. The effect of temperature on the ethylbenzene and styrene yield (β) on the AP catalyst: 1 — styrene yield; 2 — ethylbenzene yield
Рис. 1. Влияние температуры на выход этилбензола и стирола (β) на катализаторе AP: 1 - выход стирола; 2 - выход этилбензола

The second type of catalysts for the VCH dehydrogenation to styrene is the industrial iron oxide-chromium-potassium catalyst K-28. The reaction has been carried out at the temperatures of 400-600 °C, and ethylbenzene is mainly formed at the temperature of 400-500 °C, and styrene — at 500-580 °C.

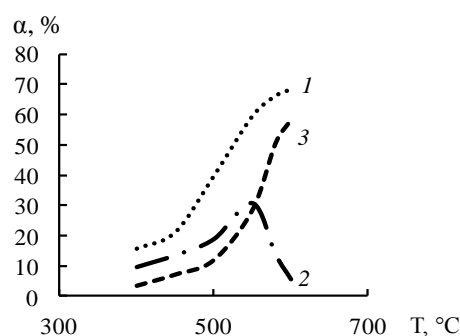


Fig. 2. Conversion (α) of VCH on the catalyst K-28: 1 — VCH conversion; 2 — ethylbenzene yield; 3 — styrene yield
Рис. 2. Конверсия (α) винилциклогексана на катализаторе K-28: 1 — конверсия винилциклогексана; 2 - выход этилбензола; 3 - выход стирола

Thus, at temperatures of 450-580 °C, ethylbenzene and styrene are formed from the initial transformed feedstock. Obviously, there is a consequential reaction of the transformation of VCH into styrene through the intermediate formation of ethylbenzene

(Fig. 2). Up to 500-550 °C, a practically uniform increase in the concentration of ethylbenzene and styrene in the dehydrogenation contact gas is noticeable. After 550 °C, the concentration of ethylbenzene in the contact gas, reaching a value of 30% by weight, begins to decrease (the curve bends), and the concentration of styrene rises sharply, reaching a maximum of 55-58% by weight at the temperature of 580-600 °C.

When conducting the experiment, the feed rate of the raw material to the reactor is of great importance. With an increase in the contact time a decrease in the feed rate of the raw materials from 0.35-0.45 to 0.15-0.20 g/g of a catalyst, the VCH conversion is tripled.

The yield of styrene to the skipped VCH, taking into account the losses in the presence of K-28 catalyst, reaches 50-60%. In this case, the highest conversion of butadiene dimers is 68.5% of the mass compared to other types of catalysts. The mileage of the catalyst before coke burning-off exceeds 0.5 h.

For the first time, the use of *Houdry's* alumina chromium catalyst in the synthesis of styrene by VCH dehydrogenation was tested. It has been established that at the catalyst operating temperatures of 500-550 °C, VCH completely turns into ethylbenzene (75.23% by weight) [18].

The process of butadiene-1,3 dimerization on a continuous flow-through installation has technological advantages compared to a batch one: the simplicity of the process equipment, the possibility of carrying out the process in a furnace coil or a heat exchanger; low pressure in the reactor; high performance; no additional solvent reagents. The calculations show a decrease in the cost of styrene produced by the synthesis and dehydrogenation of 4-vinylcyclohexene-1, relative to the self-cost of styrene obtained by ethylbenzene de-

hydrogenation, by 16.92%, which significantly increases the economic efficiency of production [19].

However, it should be noted that during the operation it is necessary to flush the reactor periodically from the accumulated resins, and in the case of a strong resinification – to burn fresh resins and polymers with subsequent passivation of the reactor metal.

Obviously, when choosing the optimal process parameters and developing a basic technological scheme of styrene production from butadiene in the second stage of styrene production from VCH, the already known dehydrogenation method on the iron-chromium-potassium catalyst K-28 in the presence of water vapor should be followed.

CONCLUSION

The process of butadiene-1,3 cyclodimerization has been studied under the laboratory conditions on batch and continuous installations. For the first time, the regularities of the butadiene thermal dimerization process in the gas phase on a flow-through installation have been established.

The process of butadiene dimers (4-vinylcyclohexene-1 and cyclooctadiene) dehydrogenation has been investigated under the laboratory conditions on a continuous flow-through installation using three types of catalysts.

The selectivity of the process for ethylbenzene has been revealed for the first time when dehydrating raw materials on the aluminum chromium catalyst.

Optimal conditions have been selected for the styrene production from butadiene-1,3 by means of a sequential synthesis of butadiene-1,3 (4-vinylcyclohexene-1 and cyclooctadiene) cyclodimers in the first stage and styrene in the second stage.

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