SovietRxiv

Soviet-era science, translated into English

CHEMISTRY

Academician A. A. BALANDIN, O. K. BOGDANOVA, and A. P. SHCHEGLOVA

1958

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-195801.35611

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

CHEMISTRY

Academician A. A. BALANDIN, O. K. BOGDANOVA, and A. P. SHCHEGLOVA

PREPARATION OF ISOPRENE BY CATALYTIC DEHYDROGENATION OF ISOPENTENES

Solving the problem of isoprene polymerization and obtaining isoprene rubber with properties superior to those of natural rubber raises the task of developing a method for the synthesis of isoprene. The cheapest and most promising raw material for obtaining isoprene may be petroleum and its refining products. In the petroleum industry there are considerable reserves of isopentane and isopentenes, which can be used to obtain isoprene by catalytic dehydrogenation.

According to the literature data ([1-4]), dehydrogenation of isopentenes with dilution by steam is carried out at a temperature of 635–650°, at a space velocity of 319–476 volumes per volume of catalyst per hour, and with dilution by steam in a ratio of 1 : 7.5–18.8 volumes. The yields of isoprene under these conditions are 35% based on the feed passed and 65–74.5% based on the decomposed isopentenes. The reaction is carried out for one hour, followed by 1 hour of catalyst regeneration.

We studied the catalytic dehydrogenation of isopentenes. To find the optimal reaction conditions, experiments were conducted at different temperatures and feed rates of isopentenes and with dilution by steam. Steam, as a diluent, has the advantage that, in addition to lowering the partial pressure of the hydrocarbon, it can serve as a heat carrier, is easily separated from the reaction products, and, moreover, steam removes carbonaceous deposits from the catalyst and thereby significantly lengthens the duration of catalyst operation without regeneration.

The amylenes for the experiments (a mixture of isomers, b.p. 21–37°) were prepared by dehydration of isoamyl alcohol over alumina and purified by distillation on a 60 theoretical-plate column. The experiments were carried out by the flow method. The apparatus was the same as in ([5]). The starting hydrocarbons were supplied from a cylinder. The feed rate was regulated by a needle valve and monitored with a rheometer. Before entering the furnace, the isopentene vapors were saturated in a saturator with steam in the required ratio. The reaction products leaving the furnace entered a receiver with a reflux condenser, where the water vapors condensed and were collected in a trap placed in a Dewar vessel and cooled with a mixture of CO_2 in acetone. The exit gas was collected in a gasometer over saturated NaCl solution. Gas volumes were reduced to normal conditions. The collected gas was analyzed in a modified Orsat–Eger apparatus.

SovietRxiv

The isoprene content in the condensate was determined using maleic anhydride. The sum of unsaturated and saturated hydrocarbons was determined in the gas phase obtained by evaporating a weighed portion of the condensate in a stream of nitrogen into a cylindrical gasometer over saturated NaCl solution. The concentration of hydrocarbons in the gas was maintained at no more than 15–16% to avoid their condensation.

The influence of temperature, feed rate, and degree of dilution with steam on the yield of isoprene was investigated. The results of experiments on the influence of temperature (540–635°) on dehydrogenation at different space velocities are given in Table 1. With an increase in temperature from 540

Table 1

Dehydrogenation of isopentenes at various temperatures and space velocities

Experiment no.	Temperature, °C	Feed rate of isopentenes, C_5H_{10} ml/l h	Dilution with steam, wt / H_2O	Yield of isoprene*, wt. % of isopentene passed	Gas analysis, vol. % CO_2	Gas analysis, vol. % C_4	Gas analysis, vol. % C_2H_4	Gas analysis, vol. % H_2	Gas analysis, vol. % CH_4	Gas analysis, vol. % C_2H_6
57	540	5000	1 : 2.7	18.4	1.8	0.8	—	95.2	2.2	—
96	540	6050	1 : 2.2	14.3	2.2	0.8	—	94.4	2.6	—
88	540	6500	1 : 2.9	12.3	1.0	0.8	—	95.4	2.7	—
63	560	3500	1 : 3.0	21.2	2.8	0.4	0.4	93.8	2.6	—
66	560	4400	1 : 2.9	22.9	2.6	0.6	0.4	94.0	2.4	—
93	560	6500	1 : 2.5	19.4	2.6	0.6	0.4	94.2	2.2	—
84	560	8500	1 : 3.0	14.9	2.2	0.6	0.2	94.6	2.3	—
61	580	3900	1 : 2.9	25.7	4.8	0.5	0.8	89.6	4.4	—
65	580	4700	1 : 2.4	26.4	4.6	0.4	0.4	90.2	4.3	—
47	580	5600	1 : 2.9	27.4	3.8	0.8	0.2	92.0	3.2	—
85	580	7200	1 : 3.2	24.5	3.0	1.2	0.2	92.0	3.5	—

SovietRxiv

Experiment no.	Temperature, °C	Feed rate of isopentene, ml/l·h	Dilution with steam, C_5H_{10} wt / H_2O	Yield of isoprene*, wt. % of isopentene passed	Gas analysis, vol. % CO_2	Gas analysis, vol. % C_4	Gas analysis, vol. % C_2H_4	Gas analysis, vol. % H_2	Gas analysis, vol. % CH_4	Gas analysis, vol. % C_2H_6
92	580	8100	1 : 2.2	25.6	2.4	1.0	0.2	94.0	2.3	–
58	600	4920	1 : 2.6	30.6	6.3	2.6	1.6	86.4	2.1	1.0
43	600	6700	1 : 3.0	31.5	4.0	0.8	0.2	91.4	3.7	–
91	600	7300	1 : 2.4	31.4	3.4	0.8	0.2	92.0	3.6	–
83	600	7800	1 : 3.0	30.0	3.0	0.8	0.1	93.0	3.1	–
55	620	5560	1 : 2.5	29.1	6.4	1.2	1.2	81.6	6.1	2.4
81	620	6660	1 : 3.2	32.8	6.4	1.4	0.6	85.6	5.8	–
103	620	7900	1 : 2.5	35.8	5.6	0.6	0.6	87.6	5.4	–
95	620	8100	1 : 2.2	36.4	6.0	1.0	0.6	86.8	5.6	–
50	635	5800	1 : 2.4	26.4	8.2	2.3	2.3	72.2	12.1	2.8
156	635	6370	1 : 2.9	25.5	7.6	2.7	2.1	73.2	12.0	2.4
112	635	8000	1 : 2.3	26.2	6.4	1.2	1.2	79.2	10.0	2.0

* The yields of isoprene based on reacted isopentenes, depending on the space velocity, were: at 540° 95-97 wt.%; at 560° 93-96 wt.%; at 580° 90-94 wt.%; at 600° 88-93 wt.%; at 620° 84-90 wt.%; at 635° 74-84 wt.%.

Up to 600° and at a space velocity of ~5000 ml/l · h, the yields of isoprene increase from 18.4 to 30.6%. At the same space velocity, at 620° the yields of isoprene are 29%, and at 635° they are 26.4%. Figure 1 shows the dependence of isoprene yields on temperature.

Fig. 1. Effect of temperature on the yield of isoprene at different space velocities: 1 –5600 ml/l · h, 2 –6700 ml/l · h, 3 –7900 ml/l · h

SovietRxiv

Fig. 1. Effect of temperature on the yield of isoprene at different space velocities: 1 –5600 ml/l · h, 2 –6700 ml/l · h, 3 –7900 ml/l · h

Figure 1: Fig. 1. Effect of temperature on the yield of isoprene at different space velocities: 1 –5600 ml/l · h, 2 –6700 ml/l · h, 3 –7900 ml/l · h

Fig. 2. Effect of space velocity on isoprene yields at different temperatures: 1 –560°, 2 –580°, 3 –600°, 4 –620°

Figure 2: Fig. 2. Effect of space velocity on isoprene yields at different temperatures: 1 –560°, 2 –580°, 3 –600°, 4 –620°

Fig. 2. Effect of space velocity on isoprene yields at different temperatures: 1 –560°, 2 –580°, 3 –600°, 4 –620°

The effect of feed rate on the process was studied in the same temperature interval, with the feed rate of isopentenes varied from 3500 to

8100 ml/l · h. From Table 1 it is seen that at 540-560° the maximum isoprene yields shift toward lower rates. At a temperature of 580-600°, varying the feed rate from 4300 to 7800 ml/l · h has little effect on the isoprene yields; at 600° the isoprene yields vary from 29.7 to 31.4% of the feed passed and from 88 to 92% of the reacted isopentenes (Fig. 2).

With increasing temperature, the yield maximum shifts toward higher feed rates, since with increasing temperature the thermal conversion of isoprene is markedly accelerated. At a feed rate of 8100 ml/l · h and at 620°, the isoprene yield reaches 36.4% of the isopentenes passed.

To determine the influence of the degree of dilution with steam on the process, two series of experiments were carried out at 560 and 580° and at a feed rate of 6500 ml/l · h. The dilution of the isopentenes with steam was varied from 1 : 1.2 to 1 : 4.2 (by weight).

Fig. 3. Effect of the degree of dilution with steam on the isoprene yield at temperature:
1 –560°, 2 –580°

As is seen from Fig. 3, the maximum on the curves corresponds to dilution of the isopentenes with steam in the ratio 1 : 2.3-3.3 (by weight). With a decrease in the degree of dilution, the formation of light hydrocarbons and CO_2 increases and the isoprene yield decreases. In experiments carried out without dilution, the isoprene yields are only 8.6% at 580° and 7.4% at 560°.

Thus, the best conditions for the dehydrogenation of isopentenes to isoprene are: temperature 580-620°, feed rate 5000-8000 ml per liter of catalyst per hour, and dilution with steam in the ratio 1 : 2.3-3.3 (by weight). The process can be conducted for a long time without regeneration of the catalyst.

Table 2

SovietRxiv

Dehydrogenation of isopentenes at a temperature of 600°, feed rate 7000 ml/l · h, and dilution with steam in the ratio 1 : 3 (by weight)

Catalyst C_5H_{10} passed, g	Coke formed, g	Contact gas, l (n.t.p.) CO_2	CH_4	C_2H_4	C_4H_8	C_4H_6	C_5H_8	C_5H_{10}	C_5H_{12}	Degree of conversion of C_5H_{10}, %	Isoprene yield on feed passed, wt. %	Isoprene formed, %	CO_2	C_2H_4	C_4	H_2	CH_4
46.3	45.8	0.29	0.3	0.1	1.4	0.2	28.2	69.2	0.5	30.7	91.3	4.9	4.4	0.4	1.6	89.4	4.2
44.4	44.0	0.23	0.3	0.1	1.6	0.2	28.8	68.6	0.2	31.4	91.7	4.8	3.4	0.4	1.0	90.6	4.6

Balanced experiments were also carried out at 600° and at an isopentene feed rate of 6700–7200 ml/l · h with dilution by steam in the ratio 1 : 3 (by weight). The duration of the experiments was 2–3 h. The results are presented in Table 2. The contact gas consists of hydrogen (89–90%) with small amounts of CO_2, C_2H_4 (0.4%), C_4 hydrocarbons (1.6%), and CH_4 (4.2%). The degree of decomposition of isopentenes per pass is 30–31.5%. Along with the main reaction of dehydrogenation of isopentenes to isoprene, with a yield of 28.8–28.2% of the feed passed and 91.3–91.7% of the decomposed isopentenes, a demethanation reaction proceeds with formation of butylene and butadiene (1.6% in total), hydrogenation of isopentenes to isopentane (0.4%), and decomposition of isoprene with formation of light gases and carbon dioxide (0.3%). Carbon dioxide is formed as a result of the interaction of carbonaceous deposits on the catalyst with steam according to the reaction: $C + 2H_2O = 2H_2 + CO_2$.

The kinetics of the reaction of dehydrogenation of isopentenes to isoprene was also studied. The experiments were carried out in the temperature range 530–590, at a rate

at a throughput of 7000 ml/l · h with dilution by water vapor in a ratio of 1 : 3 (by weight). We found that at 560° the adsorption coefficients of isopentene and of the reaction products—hydrogen and isoprene—calculated by formula (5):

$$z = \frac{\frac{m_0}{m} - 1}{\frac{100}{p} - 1},$$

are in the ratio 1 : 0.8 : 3.55, i.e., isoprene is adsorbed on the catalytically active surface more strongly than isopentene, while hydrogen is adsorbed almost the same as isopentene; with increasing temperature the relative adsorption coefficient of hydrogen does not change, while that of isoprene decreases to 2.8 at 580°. The reaction-rate constant, calculated by formula (5):

SovietRxiv

$$\frac{dx}{dt} = K \cdot \frac{[A_1]}{[A_1] + z_2[A_2] + z_3[A_3]},$$

changes from 4.3 ml/min at 530° to 12.25 ml/min at 590°. The activation energy of the dehydrogenation reaction is 23.3 kcal/mol.

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
7 III 1958

REFERENCES CITED

[1] A. Grosse, Ch. E. Morrell, J. M. Mavity, Ind. and Eng. Chem., **32**, 309 (1940).
[2] J. M. Mavity, E. E. Zetterholm, Trans. Am. Inst. Chem. Engs., **40**, 473 (1944).
[3] USA Pat. 2440471 (1948); Chem. Abstr., **42**, 5464 (1948).
[4] USA Pat. 2442319 (1948), Chem. Abstr., **42**, 6106 (1948).
[5] A. A. Balandin, O. K. Bogdanova, A. P. Shcheglova, Izv. AN SSSR, OKhN, **1946**, 497; **1955**, 723.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.