ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1117−1122. © Pleiades Publishing, Ltd., 2009.
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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Processes of Synthesis of 1-Butene from 2-Butene by the Positional Isomerization on Sulfocation Exchangers

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Received October 18, 2008

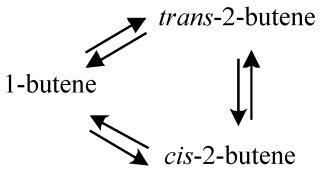
Abstract—- Obtaining of individual 1-butene and 2-butenes from the butane–butene fractions can be processed sufficiently effectively by combining positional isomerization of alkenes on the sulfocation exchanger catalysts and careful rectification. At 50–60°C is reached the equilibrium with the ratio of the sum of 2-butenes to 1-butene ~20:1. The relatively high-boiling 2-butenes are enough completely separated by rectification of 1-butene, and isobutane from the harmful impurities (butadiene and isobutene). The reverse isomerization of the purified 2-butene into 1-butene with the continuous distillation of the latter makes it possible to obtain pure 1-butene with a very low prime cost.

DOI: 10.1134/S1070427209060378

1-Butene is a very effective monomer for obtaining the high-octane fuel, and the demand for it strongly grows. 2-Butenes are of significant interest for obtaining 1,3-butadiene on the basis of their epoxidation with the subsequent dehydration of the epoxide, and for some other syntheses. Earlier used the process of obtaining butenes, in particular of 1-butene, by the dimerization of ethylene on the organometallic catalysts is complicated and expensive [1]. Obtaining 1-butene and 2-butene from the C_4-fractions of the thermal and thermocatalytic transformation of the petroleum hydrocarbons (pyrolysis, catalytic dehydrogenation and catalytic cracking) is much more attractive. In the fractions indicated the 1-alkenes and 2-alkenes are contained in the comparable quantities, the ratio is from 1.5 : 1 to 1 : 2. Their separation by the usual rectification prevents the formation of numerous azeotropes and the presence of almost tangential zeotropes [2].

Table 1 gives the data on the azeotropy and almost tangential zeotropy in the systems of 1-butene and 2-butenes. It follows from the data on the phase equilibrium and azeotropy that 2-butene can be isolated by rectification from all butanes, butene and 1,3-butadiene, except *n*-butane with which *trans*-2-butene forms azeotrope and *cis*-2-butene shows almost tangential zeotropy. The isolation of pure 1-butene from the C_4-fraction by rectification is very difficult since it forms azeotrope with isobutene and has almost tangential zeotropy with 1,3-butadiene admixtures, whose permissible content in the 1-butene for the polymerization is strictly limited, and it also has almost tangential zeotropy with isobutane. The isolation of 1-butene requires application of the complex enough technological scheme that includes, besides the effective rectification, the hydrogenation of 1,3-butadiene, removal of isobutene by chemical reaction with an alcohol with the subsequent extraction and recovery of the corresponding alcohol, and separation from isobutane by extractive rectification with a polar agent, or loss with isobutane of the substantial part of 1-butene.

We developed new technology which makes it possible to simplify substantially the isolation and purification, moreover it allows if necessary to pass all the *n*-butenes contained in the C_4-fraction either to obtaining 2-butenes or (that is particularly important) to obtaining 1-butene. The technology combines liquid-phase positional isomerization at moderate temperatures and effective rectification. At the positional isomerization of alkenes occur the following reactions (1) [3]:



(1)

In the presence of sulfocation exchangers, the reaction of the positional isomerization of *n*-butenes proceeds readily at the temperature of 50–60°C. Under the temperature conditions indicated, the equilibrium of reactions is strongly shifted to the formation of 2-alkenes, moreover in a greater extent at the lower the temperature. Experimental data on the equilibrium of the positional isomerization of *n*-butenes are given in Table 2.

The isolation of the concentrated 2-butene (sum) from the fractions containing predominantly butane and *n*-butenes (BBF) by rectification is favorable due to the fact that the boiling points of 2-butenes are higher than that of other butanes and butenes in the BBF and of the consisted in BBF 1,3-butadiene. The transformation of 1-butene into the 2-butene has also the technological value not connected directly with their isolation in the pure form, in particular, for the improvement of the alkylate obtained by the reaction of isobutane with the *n*-butenes from the fractions of catalytic cracking and also for increase of the productivity and efficiency of separation of butanes and butenes by extractive rectification.

At the rectification, *n*-butane partially (10–20%) falls into the 2-butene. This does not have a negative effect on the catalysts of further transformation of 2-butene, and it is removed after the transformation of 2-butene into the necessary products. Acid catalysts, in this case sulfocation exchangers, simultaneously catalyze the reactions dimerization and oligomerization of alkenes:

$$\text{alkene} + \text{alkene} \xrightarrow{+\ \text{alkene}} \text{dimer}$$

$$\xrightarrow{+\ \text{alkene}} \text{trimer etc.} \qquad (2)$$

Usually, at the obtaining of alkenes the indicated reactions are undesirable. However strangely, until recently researchers attempted to carry out the positional isomerization with the concentrated alkenes, which unavoidably led to significant dimerization and oligomerization of the latter, and to deactivation of sulfocation exchanger. In actuality, the problem can be solved rather easily taking into account the fact that the isomerization reactions are monomolecular while the reactions of dimerization and oligomerizations are

Table 1. Azeotropy and the almost tangential of zeotropy in the systems formed by 1-butene and 2-butenes

Component 1	Components 2	Portions of component 2 in the azeotrope	Pressure of azeotrope, kPa	lim a_{12} $x \to 1$
Isobutane	1-Butene	Almost tangential [zeotrop]		1.05
Isobutene	1-Butene	25.0	475	
1-Butene	1.3-Butadiene	Conditionally almost tangential [zeotrop]		1.09
n-Butane	*trans*-2-Butene	28.0	381	
n-Butane	*cis*-2-Butene	Almost tangential [zeotrop]		1.02
trans-2-Butene	*cis*-2-Butene	Almost tangential [zeotrop]		1.06

Table 2. Equilibrium concentrations 1- and 2-butene at relatively low temperatures

Hydrocarbons	bp, 0°C	Concentrations in the equilibrium mixtures, %[a]						
		0°C	20°C	40°C	60°C	80°C	100°C	150°C
1-Butene	–6.3	1.8	2.5	3.3	4.1	5.0	6.0	9.8
trans-2-Butene	+0.9	72.2	69.8	65.9	62.5	59.0	55.9	49.4
cis-2-Butene	+3.7	26.0	27.7	30.8	33.4	36.0	38.1	40.8

[a] Here and further concentrations are in wt %.

respectively bimolecular or consist of series of the sequential bimolecular reaction. The isomerization of alkenes proceeds with high selectivity when is carried out in the presence of 65–80% of alkanes. Just this quantity of alkanes usually is present in many fractions of the thermocatalytic transformation of petroleum hydrocarbons, and before the carrying out the selective isomerization of alkenes the alkenes should not be preliminarily concentrated.

Often it is necessary to exclude the 1,3-butadiene from the products distilled off from the targeted 2-butene, which is dictated by the tasks of their further processing, for example, dehydrogenation. In this case before the isomerization it is expedient to perform the liquid-phase hydrogenation of 1,3-butadiene contained in the C_4-fraction. On the catalysts of hydrogenation, which in particular contain Ni or Pd on a carrier, in the presence of hydrogen simultaneously occurs the partial positional isomerization of butene. It goes slower than on sulfocation exchangers, and one should not attempt to use it for the deep isomerization because of the significant (to ~20%) hydrogenation of butenes into butanes. The regime of transformation on Ni or Pd catalysts must be determined precisely by the task of the hydrogenation of alkadienes. It is possible to reach 25–30% of the allowed (defined by the chemical equilibrium) isomerization of 1-butene into the 2-butene.

The kinetic characteristic of the conversion of 1-butene and 1,3-butadiene on the sulfocation exchangers and the catalysts of hydrogenation are given in Table 3 on the example of processing a C_4-fraction containing ~70% of butanes, 14% of 1-butene, 14.5% of 2-butene, and 1.3% of 1,3-butadiene. The sulfocation exchanger with the static exchange capacity SEC=5.1 mg-equiv/[g] was applied. For the deeper transformation of 1-butene into the 2-butenes it is possible to separate preliminarily by rectification the contained in the BBF 2-butenes. The conversion of 1-butene into the 2-butenes reaches:

– 90–91% without the preliminary rectification of BBF for the separation from 2-butenes,

– ~96% when preliminary rectification of BBF for the separation from 2-butenes was carried out.

Isomerization for the improvement of cracking alkylate. An increase of the 2-butenes : 1-butene ratio in the flow passed for the alkylation (reaction with isobutene) leads to increase in the fraction of 3-methylpentanes in the alkylate and increase in its RON by 1.5–3 points. This to the greatest degree occurs in the processes of alkylation with the use HF. Helpfully the alkylation *n*-butenes + isobutane is carried out with the 7-fold excess of isobutene, and unreacting isobutane is recirculated and mixed with BBF. This situation is convenient for the carrying out the 1-butene to 2-butenes isomerization on the sulfocation exchangers.

In the mixed flow the butane content exceeds 80–85%, which practically excludes essential dimerization and oligomerization of *n*-butenes. The block-scheme of the process of alkylation preceded by isomerization is shown in Fig. 1.

Isomerization for increasing in productivity and efficiency of BBF separation by extractive rectification. At the separation of butanes from *n*-butenes during the separation of butane–butane fractions (BBF) by the extractive rectification (with acetonitrile, *N*,*N*-dimethylformamide (DMF) or another polar extractant) the most hardly separable ("determining") pair is the pair *n*-butane–1-butene. At the extractant concentration (acetonitrile, DMF) 70 wt. % the coefficient of the relative volatility α_{12} of this pair is 1.25. After the transformation of main quantity of 1-butene into the 2-butene the "determining" one becomes the pair *n*-butane–*trans*-

Table 3. Kinetic data on the conversion of 1-butene and 1,3-butadiene

Hydrocarbons	Conversion in the C_4-fraction					
	sulfocationite, 20% 60°C			Ni/keselguhr, 20% 60°C		
	2 h	4 h	5 h	2 h	4 h	5 h
1-Butene	72.1	88.6	91.5	69.0	90.7	92.8
Butadiene(s)	15.0	30.8	38.5	89.0	96.2	~100
Butenes into *n*-butane	–	–	–	8.4	17.2	21.4
Formation of dimmers, %	0.4	0.8	1.0	–	–	0.05

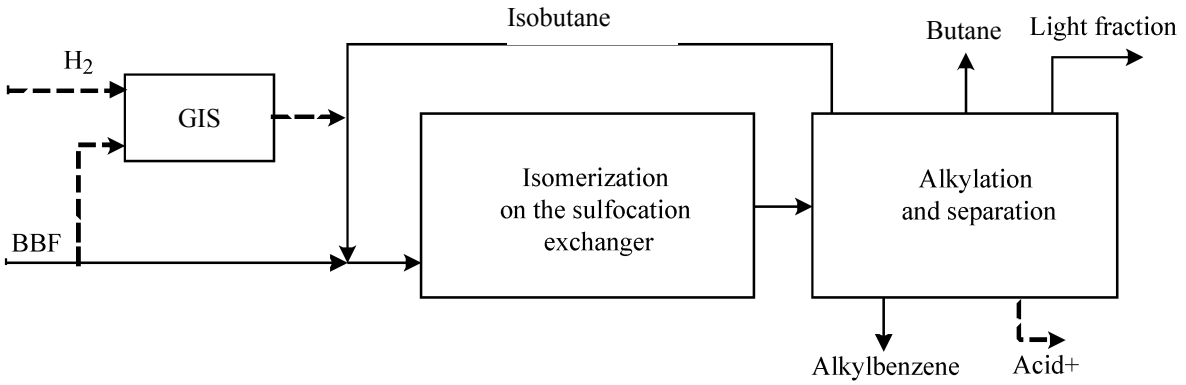


Fig.`1. Scheme of positional isomerization in combination with obtaining of cracking-alkylate.

2-butene (under the same conditions $\alpha_{12} = 1.56$). This effect is achieved because the boiling points of *n*-butane, 1-butene, *trans*-2-butene and *cis*-2-butene are –0.5°C, 6.9°C, +0.9°C and +3.7°C respectively, and after isomerization the *n*-butane is separated in the process of extractive rectification not from 1-butene, but from the higher boiling 2-butene. The scheme of process is shown in Fig. 2. Before the unit of extractive rectification can be mounted a simple adiabatic reactor with sulfocation exchanger, which practically not consumes additional power (the hydroisomerization is not always necessary). As a result, the productivity of the unit of extractive rectification grows twice, and the power consumption in it is reduced 2.3-fold. If necessary, this method makes it possible to use the less expensive extractants in the extractive rectification not contaminating the mixture with ammonia or amines, for example methylethylketone.

Obtaining of concentrated 2-butenes. The concentrated 2-butenes (sum) can be isolated from BBF by the usual (effective) rectification as the bottom residue (with the admixture of *n*-butane). This, however, does not make it possible to inolve 1-butene to the obtaining 2-butenes. But this involvement can be very useful at the producing 1-butene with the reverse isomerization of 2-butenes and at the producing 1,3-butadiene by the epoxidation of 2-butenes and decomposition of the epoxide. For the involvement practically entire potential of *n*-butenes into the obtaining of 2-butenes is carried out isomerization of 1-butene into 2-butene in BBF with the subsequent rectification as shown on the left side of Fig. 3 (IS-1 and K-1). For more complete removal of 1,3-butadiene before the isomerization on sulfocation exchanger (IS-1) it can be carried out the liquid-phase hydroisomerization (GIS). If necessary, the content of isobutene and 1,3-butadiene in the 2-butene can be reduced to the level of less than 0.001%. Temperature in the IS-1 is 50–60°C. As the catalyst is used any sulfocation exchanger, preferably fine-grained, with COE > 3.0, but is better with COE above 4.0. In GIS (if included) the temperature is ~60°C and is used any

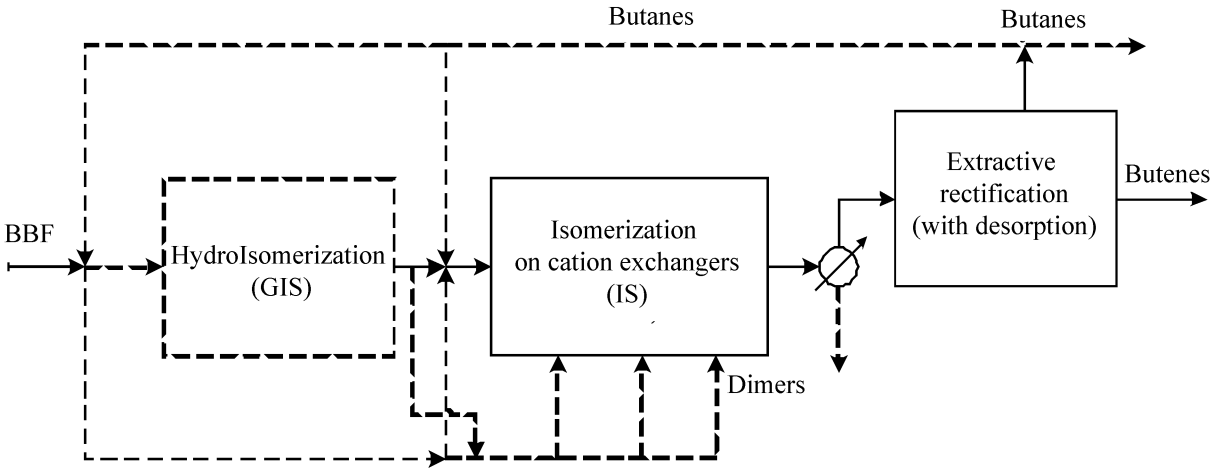


Fig. 2. Scheme with the use of isomerization for increasing the productivity of the extractive rectification.

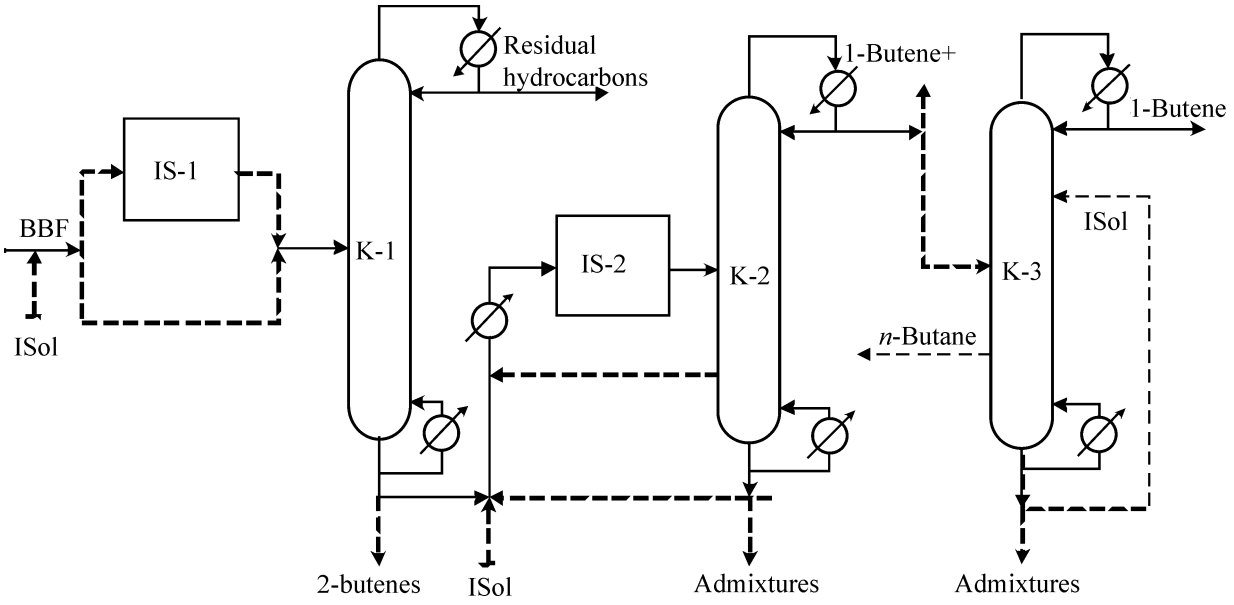


Fig. 3. Scheme of obtaining pure 1-butene from the hydrocarbon mixtures with the use of isomerization in the direct-flow reaction zones. (IS-1) the unit of the isomerization of 1-butene into the 2-butene; (IS-2) the unit of the isomerization of 2-butene into the 1-butene; (K-1, K-2, K-3) rectifying columns; (ISol)is inert solvent.

suitable hydrogenating catalyst: Ni/kieselguhr, Pd/Al_2O_3, etc. The conversion of 1-butene into the 2-butene achieves 91–96%. As the admixture in the 2-butene is contained *n*-butane (10–20%).

Obtaining of 1–butene. The method of obtaining 1-butene consists of the isomerization in BBF of 1-butene into 2-butenes, removal of isobutane, isobutene and 1,3-butadiene from the 2-butenes by effective rectification and then reverse isomerization of 2-butenes into the 1-butene with the separation of the latter by rectification. This technological solution at first glance seems paradoxical. In actuality this process is the most simple and effective. It gives rise to use practically entire potential of *n*-butenes contained in BBF for obtaining the pure 1-butene. The content of 1,3-butadiene and isobutene in the final 1-butene is identical with the attainable in the 2-butene, i.e., less than 0.001%. At the primary distilling off (with rectification) of 1-butene from the reaction mixture after IS-2 the content of *n*-butane in the butene is 10–20%. If necessary 1–butene (1) is further separated from *n*-butanes (2) by the effective rectification (α_{12} = in the 1-butene excess is 1.1) or, that is more preferable, by rectification in the presence of a higher boiling alkane, for example in *n*-pentane or isopentane (in this case α_{12} = 1.3). The scheme of process is given in Fig. 3. In IS-2 is used more thermoresistant sulfocation exchanger (for example, Amberlist-36 or DS) and higher temperature (130–160°C) is maintained. The conversion of 2-butene into the 1-butene for one passage is 9–13%. Because of the recirculation of liquid flow from the bottom or the lower part of K-2 to IS-2 the total conversion of 2-butene into the 1-butene in this process reaches 99–100%.

As a result of rectification in K-2 the distillate obtained contains 80–90% of 1-butene and 10–20% of *n*-butane and if necessary less than 0.001% admixed 1,3-butadiene and isobutene. At the use of rectification in K-3 the distillate contains 98–99% of 1-butene and 1–2% of *n*-butane (content of the above indicated admixtures is less than 0.001%). From 1 ton of BBF containing 30–50% of *n*-butenes is produced 0.27–0.45 ton of 1–butene. The organization of producing 1-butene by the proposed method is very profitable. The prime cost of the obtained 1-butene is 16–17 thousands rubles per 1 ton, while its market price is over 50 thousands rubles per 1 ton. The raw material (BBF) is available in an excess quantity, and the process is sufficiently simple. With power 100 000 ton/year the annual economic effect is over 3 billion rubles. The realizations of 1-butene are favorable both in Russia and as the export product. The technology of the polymerization of 1-butene is similar to that of the stereoregular polymerization of 1,3-butadiene and isoprene (it is carried out with the use of $TiCl_4$). Apparently, the realization of the production of 1-butene and its polymer can guarantee profitability of the Efremov and Yaroslavl plants of synthetic rubber

which were proven to be in the difficult situation because of the shortage of the monomers, 1,3-butadiene and isoprene, and also it is completely effective for the number of other enterprises.

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