ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1128−1132. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © O.S. Pavlov, S.A. Karsakov, S.Yu. Pavlov, 2009, published in Khimicheskaya Promyshlennost', 2009, Vol. 86, No. 1, pp. 71−76.

TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

The Process of Producing 2-Methyl-2-butene by Positional Isomerization on Sulfocation Exchangers

O. S. Pavlov, S. A. Karsakov, and S. Yu. Pavlov

Yaroslavl State Technical University, Yaroslavl, Russia
e-mail: olefin@mail.ru
Scientific and Technological Center of Chemical Technologies, Yaroslavl, Russia

Received November 14, 2008

Abstract—-The results of determination of composition and strength of the granules of nitrogen-phosphoric fertilizers containing 1.5 to 5.0% of P_2O_5, obtained by interaction of the mineralized mass of the phosphorites of Central Kyzylkum with the 70–90% solutions of ammonium nitrate at 110°C, are presented.

DOI: 10.1134/S1070427209060391

Economical producing of 2-methyl-2-butene is an important element of the promising process of the production of isoprene by epoxidation of 2-methyl-2-butene and dehydration of the formed epoxide. The effective method of the production of 2-methyl-2-butene is dehydrogenation of isopentane and subsequent obtaining of 2-methyl-2-butene from the formed C_5-fractions by liquid-phase isomerization of 2-methyl-1-butene, preferably on sulfocation exchangers followed by isolation of 2- methyl -2-butene from the formed C_5 fractions by usual rectification.

The proposed process makes it possible to decrease sharply the capital investments for the reconstruction of the existing production of isoprene from isopentane in comparison with the OKSEP process [1] based on the oxidation of isopentane.

The raw material for obtaining 2-methyl-2-butene is the C_5- fractions of the thermal or thermocatalytic transformation of petroleum hydrocarbons, from which the most accessible and convenient for the processing are the fractions of the catalytic dehydrogenation of isopentane. The process of the isopentane dehydrogenation is achieved in the gas phase at ~600°C. It is relatively not expensive. The conversion of isopentane, predominantly into isopentenes, is ~ 40%. The ratio 2-methyl-1-butene : 2-methyl-2-butene : 3-methyl-1-butene in them is approximately 1 : 1.9 : 0.15; normal boiling points of these isobutenes are respectively 31.2°C, 38.6°C and 20.1°C. Their separation by rectification does not a problem.

The transformation of the larger part of 2-methyl-1-butene into 2-methyl-2-butene in the C_5-fractions can be achieved by application of a comparatively simple method: by liquid-phase positional isomerization n the basis of reaction (1):

$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2{-}CH_3 \rightleftharpoons CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{-}CH_3 \qquad (1)$$

This reaction proceeds sufficiently easily in the presence of sulfocation exchanger catalyst at a temperature from 10 to 40°C. At these temperatures the equilibrium of reaction is strongly shifted to the side of the formation of 2-methyl-2-butene, the greater at the lower temperature. Experimental data on he equilibrium of the reaction of the positional isomerization of 2-methyl-1-butene into 2-methyl-2-butene are given in Table 1.

Besides the acidic (sulfocation exchanger) catalysis for the positional isomerization of 2-methyl-1-butene into 2-methyl-2-butene can be used the catalysts containing nickel, palladium, cobalt or platinum, in the presence of a small quantity of hydrogen. A disadvantage of the catalysis by this method is relatively slow conversion and a significant hydrogenation of isopetenes into isopentane. On the other hand, in the case of presence of

Table 1. Equilibrium concentrations at the isomerization of 2-methyl-1-butene and 2-methyl-butene at relatively low temperatures

Hydrocarbons	Concentration in the equilibrium mixtures, %[a]					
	0°C	20°C	40°C	60°C	80°C	100°C
2-methyl-1-butene	4.1	6.2	8.5	10.4	12.7	15.9
2-methyl-2-butene	95.9	93.8	91.5	89.3	87.3	84.1

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

pentadienes (isoprene, piperylenes) in the C_5-fractions, their hydrogenation into pentenes (and possibly into pentanes) can be very useful for the exception of the adding of isoprene to isopentane, because at the further recirculation for the dehydrogenation it should be excluded to avoid coking and deactivation of catalyst of dehydrogenation, and also for the exception of entry in 2-methyl-2-butene of piperylenes, which adversely affect the process of the epoxidation of 2-methyl-2-butene and the quality of isoprene, obtained from the epoxide. In this connection can be expedient the combination of the liquid-phase hydroisomerization of the components of C_5-fraction with the subsequent isomerization in it of 2-methyl-1-butene into 2-methyl-2- butene.

In Table 2 are given kinetic data on the conversion of tertalkenes and alkadienes in the C_5-fraction containing 63.7% of pentanes (in essence of isopentane), 10.2% of 2-methyl-2-butene, 21.1% of 2-methyl-1-butene, 1.4%, of isoprene and 0.4% of piperylenes. As the catalysts are used: sulfocation exchanger with a static exchange capacity SEC = 51 mg-equiv/g and the catalyst "Ni on the kieselguhr" containing ~20–40% of nickel. The amount of hydrogen in the reaction mixture at the hydroisomerization was regulated by the maintenance of its partial pressure 3–3.5 atm (abs.).

Acid catalysts, in such cases sulfocation exchangers, simultaneously catalyze both reactions di- and oligomerizations of alkenes:

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

At the isomerization on sulfocation exchangers it is necessary to avoid the essential contribution of reactions of di- and oligomerization of pentenes and pentadienes. Rather strangely, but until recently researchers attempted to conduct the position isomerization of concentrated alkenes, which unavoidably led to their significant di- and oligomerization and deactivation of sulfocation exchanger. The problem of suppression or substantial limitation of di- and oligomerization effectively is solved taking into account the fact that the isomerization reactions are monomolecular, and reactions di- and oligomerizations are respectively bimolecular or sequential bimolecular reaction. The isomerization of alkenes proceeds sufficiently selectively in the presence of 60-80% of alkanes. Specifically, this quantity of alkanes usually is present in many fractions of the thermocatalytic transformation of petroleum hydrocarbons, and for achievement the selective isomerization of alkenes one ought not to attempt to preliminarily concentrate them. If necessary,

Table 2. Kinetic data on the conversion of *tert*-pentenes and pentadienes

Hydrocarbons	Conversion in the C_5-fraction,%					
	sulfocation exchanger, 20%, 40°C			Ni/keselguhr, 20%, 40°C		
	2 h	4 h	5 h	2 h	4 h	5 h
2M1B to 2M2B	65.7	80.4	82.4	21.0	38.1	44.8
Pentadienes	11.1	27.8	38.9	90.9	~100	~100
Isopentene to isopentane	–	–	–	3.0	6.1	7.5
Formation of dimers, %	0.5	0.8	1.0	–	–	≤0.05

Table 3. Characteristic of azeotropy and almost tangential zeotropy in the binary systems formed by pentanes, isopentanes and pentadienes

Component 1, bp, °C	Component 2, bp, °C	Azeotropy		Almost tangential zeotrop	
		component 2, wt %	bp of azeotrope,°C	presence	α_{12} in excess of component 1
3M1C, 20.1°C	Isopentane, 27.8°C	–	–	–	1.24
Isopentane, 27.8°C	2M1B, 31.2°C	–	–	+	1.05
Isopentane, 27.8°C	Isoprene, 34.1°C	–	–	+	1.04
Isopentane, 27.8°C	2M2B, 38.6°C	–	–	–	1.36
Isopentane, 27.8°C	Cyclopentadiene, 41.5°C	–	–	–	1.20
2M1B, 31.2°C	Isoprene, 34.1°C	–	–	+	1.05
2M1B, 31.2°C	*n*-Pentane, 36.1°C	–	–	–	1.10
2M1B, 31.2°C	2M2B, 38.6°C	–	–	–	1.20
Isopren, 34.1°C	*n*-Pentane, 36.1°C	26.0	33.8	–	1.11
Isopren, 34.1°C	2M2B, 38.6°C	–	–	–	1.12
Isopren, 34.1°C	Cyclopentadiene, 41.5°C	–	–	–	1.14
2M2B, 38.6°C	*trans*-Pentadiene, 42.0°C	–	–	–	1.11
2M2B, 38.6°C	*cis*-Pentadiene, 44.1°C	–	–	–	1.19
2M2B, 38.6°C	Cyclopentadiene, 41.5°C	–	–	+	1.08

alkene concentration can be increased by their additional introduction or recovery of isopentane fraction, distilled off from 2-methyl-2- butane.

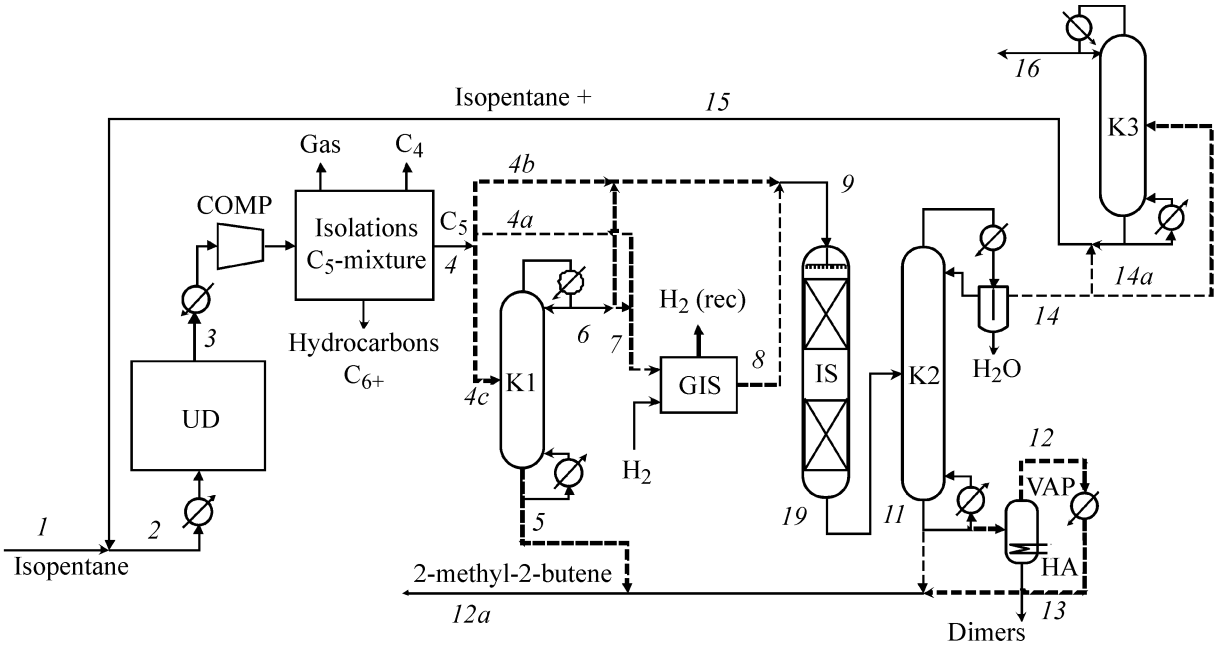
For increase of the conversion of 2-methyl-1-butene into 2-methyl-2-butene the preliminary distillation of C_5-fraction from 2-methyl-2-butene can be used before the isomerization.

The distillation (rectification) of pentanes, isopentanes and isoprene from 2-methyl-2-butene does not cause essential difficulties, with exception of distilling *n*-pentane from it and distilling 2-methyl-2-butene from *trans*-1.3-pentadiene. The distillation of isopentane from 2-methyl-2-butene and isoprene is difficult, because of almost zeotropy in the systems isopentane–2-methyl-2-butene and 2-methyl-2- butane–isoprene [2, 3]. This makes necessary sufficiently deep isomerization of 2-methyl-1-butene into 2-methyl-2-butene and desirable hydrogenation of isoprene in the C_5-fraction before the isomerization, although the hydrogenation of isoprene in the isopentane fraction can be realized, also, after its distilling off from 2-methyl-2-butene.

3-Methyl-1-butene owing to its sufficiently low boiling point, 20.1°C, sufficiently easily is distilled off from all pentanes, pentenes and pentadienes. Its isolation can be of independent interest as the monomer and the comonomer for producing plastics.

Table 3 contains the characteristic of azeotropy and almost tangential zeotropy in the binary systems, formed by pentanes, isopentanes and pentadienes.

In the figure is shown a scheme of synthesis of 2-methyl-2-butene and partially of 3-methyl-1-butene from isopentane, which includes: dehydrogenation of isopentane, isolation from the contact gas of C_5-mixture containing predominantly isopentane and *tert*-pentenes, and also partially (as the admixtures) isoprene, 3-methyl-1-butene, *n*-pentane, *n*-pentenes and piperylenes (unbranched 1,3- pentadienes). Isomerization and possible hydroisomerization of 2-methyl-1-butene into 2-methyl-2-butene, is combined with the hydrogenation of pentadienes, rectification, possible revaporization of 2-methyl-2- butene, and also the distillation (rectification) of 3-methyl-1-butene from the flow of recurrent isopentane.



Syntyesis of 2-methyl-2-butene and 3-methyl-1-butene from isopentane. (UD) unit of dehydrogenation; (COMP) compressor, (GIS) hydroisomerization, (IS) isomerization on sulfocation exchanger, (K1, K2, K3) rectification columns and vaporizer, (HA) heating agent.

To the reactor of isomerization [IS] is loaded sulfocation exchanger preferably with static exchange capacity SEC ≥ 4.0, temperature in the IS is 20–30°C. It is possible (optional) the preliminary rectification of C_5-fraction from the 2-methyl-2-butene in the column K1. If additionally is used a reactor of the hydroisomerization GIZ, in it is used "hydrogenating" catalyst (preferably "Ni on the kieselguhr") and is maintained the temperature of 20–35°C. After GIZ the content in the mixture: isoprene ≤0.1%, piperylenes ≤0.01%.

The total conversion of 2-methyl-1-butene into the 2-methyl-2- butene: without use of K1 is 81.4%, with use of K1 is 93–94%, which corresponds to obtaining 90.8% and 93.3%, respectively, of 2-methyl-2-butene on

Table 4. The characteristic of the main flows at the producing 2-methyl-2-butene and possible 3-methyl-1-butene from isopentane

Hydrocarbons	Flows (composition, wt %)									
	1	2	4–7	8–9	10	11	12	14–14a	15	16
Isopentane	99.5	~96.95	67.0	~68.5	~68.6			94.1	95.75	2.0
n. Pentane	0.5	0.6	0.7	0.8	0.8	1.3	1.3	0.7	0.7	
3M1B		0.3	1.4	1.4	1.4			1.9	≤0.05	~98.0
n. Pentene		0.4	0.7	0.7	0.7	0.5	0.5	0.6	0.8	
2M1B		0.4	9.4	6.9	2.0			2.2	2.2	
2M2B		0.05	18.2	21.6	26.4	97.8	98.5	0.4	0.4	≤0.02
Isopren			2.3	≤0.01	≤0.08			≤0.1	≤0.1	
Pentadiene			0.3	≤0.01	≤0.01	≤0.05	≤0.05			
Dimers					0.1	0.4				
Flow, kg/h	1100	3246	2984	2984	2984	796	793	2188	2146	~42

the whole *tert*-pentenes contained in the mixture.

Table 4 gives the characteristic of the main flows with obtaining of 2-methyl-2-butene and 3methyl-1-butene without use of column K1, with supply of flow *11* (2-methyl-2- butene) completely into the vaporizer VAP and flow *14* completely into column K3. A numeration is the same as in Fig. 1.

The consumption of isopentane in the process is ~1.4 ton per 1 ton of obtained of 2-methyl-2- butene. Therewith it can be isolated 50 kg of 3-methyl-1-butene per 1 ton of 2-methyl-2- butene.

The process advantage is the fact that it makes it possible to conduct reconstruction of the first stage of the line for producing isoprene from isopentane without reconstruction of the blocks of the isopentane dehydrogenation and gas fractionation (isolation of C_5- fraction) of isopentane–isopentene mixtures by extractive rectification and with the possible use of the same equipment for obtaining of 2-methyl-2-butene and for the fraction of recurrent (to the dehydrogenation) isopentane, and possible 3-methyl-1-butene.

This decreases sharply the capital investments necessary for the reconstruction of the lines for producting isoprene from isopentane via their transfer from two-stage dehydrogenation of isopentane into the process with the epoxidation of 2-methyl-2-butene and the dehydration of epoxide (which gives a reduction in the prime cost of isoprene more than twice). In conjunction with the new developments for obtaining and dehydration of 2-methyl-2,3-epoxybutane this makes such reconstruction completely real.

REFERENCES

1. Pavlov, S.Yu. and Surovtsev, A.A., *Khim.Prom.*, 1997, no. 7, pp.12–19.
2. *Spravochnik neftekhimika* (Handbook of Oil Chemist), Ogorodnikov, S.K., Ed., vol. 2, Leningrad: Khimiya, 1978.
3. Pavlov, S.Yu., *Vydelenie i ochistka monomerov dlya sinteticheskogo kauchuka* (Recovery and Purification of Monomers for Synthetic Caoutchouc), Leningrad: Khimiya, 1987, pp. 11–14.