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Thermodynamic Parameters of the Single-Stage Dehydrogenation of Isopentane to Isoprene

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Abstract—From the results of experiments with platinum-containing catalysts operating in the steady mode, adiabatic changes in temperature in the course of 2-metylbutane dehydrogenation to monoolefins and isoprene were calculated. Dehydrogenation of 2-methylbutane and its mixtures with methylbutenes in the 500–600°C temperature range was simulated with varying the concentrations of 2-methylbutane, methyl-butenes, hydrogen, and water, the conversion, and the selectivities with respect to both isoprene and methylbutenes. The most suitable reactor designs with intermediate heating of the reaction mixture were suggested.

The development of high-performance catalysts for dehydrogenation of isoalkanes is a priority research field today, because production of synthetic rubbers (including isoprene rubbers) is the most developed branch of petrochemical industry in Russia and other countries [1].

Single-step dehydrogenation of isoalkanes at atmospheric pressure in the presence of bimetallic platinum-containing catalysts is a promising and economically efficient process. This process surpasses in efficiency such existing processes as two-step method of isoprene preparation, one-step procedure of vacuum dehydrogenation of 2-methylbutane, and formaldehyde synthesis of isoprene [2–5]. Significant simplification of the flowsheet due to performing the process in one-step at atmospheric pressure (i.e., without any vacuum installations) is an advantage of this procedure. The catalyst is used in a fixed bed; in so doing, its high selectivity and activity are preserved. Elimination from the process scheme of the first step of dehydrogenation with a highly toxic chromium-containing catalyst will improve the working conditions and reduce the environmental hazard. Up to now, despite a number of advantages, one-stage dehydrogenation at atmospheric pressure using bimetallic catalysts is not used in commercial production. From our viewpoint, this is due to the fact that the one-step process, owing to high endothermic effect, requires supply of significant amount of heat to the reaction zone, which is unfeasible with modern installations.

The aim of this study was to calculate the thermodynamic characteristics of one-stage dehydrogenation of 2-methylbutane to methylbutenes and isoprene and to determine the type of reactor that can be used in this case.

Data on the theoretical yields of dienes in dehydrogenation of paraffin–olefin mixtures at various pressures were presented previously in [6, 7]. However, under the real experimental conditions, the catalyzate composition can strongly differ from the theoretical data for both operation (reactor type, procedures of the reagents and heat-carrier supply, etc.) and chemical (side cracking reactions, isomerization, diene transformations, etc.) reasons. To accomplish the goal of this study, we simulated on the basis of experimental data the dehydrogenation of 2-methylbutane and its mixtures with methyl-butenes in a reactor with a fixed bed of platinum–aluminum–zinc catalyst.

The composition of the contact gas from dehydrogenation of isopentane in an isothermal laboratory reactor with a fixed bed of the catalyst that attained the steady operation mode is listed in Table 1. As can be seen, in one cycle of the single-stage dehydrogenation of 2-methylbutane using platinum–aluminum catalyst the yields of isoprene

Table 1. Composition of the contact gas and characteristics of the catalytic activity of bimetallic platinum–aluminum catalyst. Feed: 2-methylbutane, 98.57 wt %

Composition of contact gas and activity characteristics	Dehydrogenation temperature, °C			
	530	560	580	600
Composition, wt %:				
total C_2	0.24	0.53	0.62	0.97
CO_2 (recalculated to carbon)	0.65	1.89	2.51	4.23
total C_3	0.29	0.93	1.29	2.2
total C_4	2.03	4.32	4.91	6.03
2-methylbutane	40.95	31.62	30.91	33.67
n-pentane	1.01	0.13	0.07	0.01
methylbutenes	44.08	45.78	38.55	29.11
n-pentenes	0.82	0.95	0.6	0.28
isoprene	7.88	11.71	16.44	18.64
piperylene	0.45	0.85	1.34	1.31
cyclopentadiene	1.6	1.29	2.76	3.55
Catalytic parameter, wt %:				
yield of isoprene based on starting compound	7.99	11.88	16.68	18.91
yield of isoprene based on converted starting compound	13.68	17.49	24.30	28.72
yield of methylbutenes based on starting compound	44.62	46.34	39.01	29.66
yield of methylbutenes based on converted starting compound	76.33	68.23	56.83	54.66
conversion	58.46	67.92	68.64	65.84

and methylbutenes reach 18 and 40 wt % with the selectivity to unsaturated hydrocarbons of up to 91%.

The choice of the reactor with the fixed catalyst bed is primarily governed by the character of the occurring chemical reactions, determining adiabatic changes in temperature on passing of the feed through the catalyst bed. In this connection, we calculated adiabatic changes in temperature in the reactor for vapor-phase dehydrogenation of 2-methylbutane and its mixtures with methylbutenes.

In the general form, the adiabatic changes in temperature owing to changes in the reaction heat ΔT are determined by the following expression:

$$\Delta T_{ad} = T_{out} - T_{in} = \Sigma \Delta H_i / \Sigma (C_p)_j, \qquad (I)$$

where $\Sigma \Delta H_i$ is the sum of thermal effects of chemical reactions occurring in the system (taking into account conversion of the reagent and selectivity to the final products) (kJ mol^{-1}); $\Sigma (C_p)_j$ is the sum of the heat capacities of the components (taking into account conversion of the reagent, selectivity to the final products, and heat capacity of the inert heat carrier fed to the system) (kJ mol^{-1} K^{-1}).

The following reactions occur in the system in the course of isopentane dehydrogenation.

(1) Dehydrogenation of 2-methylbutane to methylbutenes, without taking into account isomerism of the monoolefins:

$$i\text{-}C_5H_{12} \rightarrow i\text{-}C_5H_{10} + H_2. \qquad (1)$$
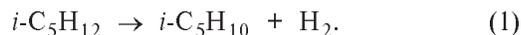
(2) Dehydrogenation of methylbutenes ($i\text{-}C_5H_{10}$) to isoprene, without taking into account isomerism of the monoolefins:

$$i\text{-}C_5H_{10} \rightarrow i\text{-}C_5H_8 + H_2. \qquad (2)$$

(3) Dehydrogenation of 2-methylbutane ($i\text{-}C_5H_{12}$) to isoprene:

$$i\text{-}C_5H_{12} \rightarrow i\text{-}C_5H_8 \text{ (isoprene)} + 2H_2. \qquad (3)$$
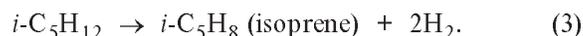
As for thermal calculations the mechanism of a chemical reaction is of no significance, chemical transformation of 2-methylbutane into isoprene can be presented as a combination of reactions (1) and (2) with 2-methylbutane as the starting reactant.

In this case, setting certain values of the total conversion of isopentane $\alpha_{isopentane}$, selectivity of 2-methylbutane dehydrogenation to monoolefins $S_{pentene}$, and selectivity of 2-methylbutane dehydro-

**Table 2.** Thermodynamic characteristics of components at various temperatures

Component	Enthalpy of formation, kJ mol⁻¹	Heat capacity, J mol⁻¹ K⁻¹
2-Methylbutane	$6.777\times10^{-5}T^2 - 1.345\times10^{-1}T - 1.206\times10^2$	$-1.756\times10^{-7}T^2 + 4.547\,10^{-4}T - 1.054\times10^{-3}$
2-Methyl-2-butene	$5.242\times10^{-5}T^2 - 1.126\times10^{-1}T - 1.389\times10$	$-1.410\times10^{-7}T^2 + 3.800\times10^{-4}T + 4.248\times10^{-3}$
2-Methyl-1-butene	$5.120\times10^{-5}T^2 - 1.063\times10^{-1}T - 9.285$	–
3-Methyl-1-butene	$4.475\times10^{-5}T^2 - 9.328\times10^{-2}T - 5.188$	–
Isoprene	$3.320\times10^{-5}T^2 - 6.917\times10^{-2}T + 9.326\times10$	$-1.639\times10^{-7}T^2 + 3.707\times10^{-4}T + 9.934\times10^{-3}$
Hydrogen	–	$33.066178 - 11.363417T\times10^{-3} + 11.432816(T\times10^{-3})^2 - 2.772874(T\times10^{-3})^3 - 0.158558(T\times10^{-3})^{-2}$
Water	–	$30.092 + 6.832514T\times10^{-3} + 6.793435(T\times10^{-3})^2 - 2.53448(T\times10^{-3})^3 + 0.082139(T\times10^{-3})^{-2}$

genation to isoprene $S_{isoprene}$, the amount of heat consumed in the course of the chemical reaction can be presented as follows:

$$\Delta H_{rea} = \Delta H_1 \alpha_{isopentane} S_{pentene} + \Delta H_3 \alpha_{isopentane} S_{isoprene},$$

where ΔH_1 and ΔH_3 are the thermal effects of reactions (1) and (3) (kJ mol⁻¹), $\alpha_{isopentane}$ is the conversion of 2-methylbutane (fraction of unity), and $S_{pentene}$ and $S_{isoprene}$ are the molar selectivities of 2-methylbutane dehydrogenation to methylbutenes and isoprene (fraction of unity).

Since dehydrogenation of 2-methylbutane yields three major isomers of monoolefins, reaction (1) can be presented as three parallel reactions:
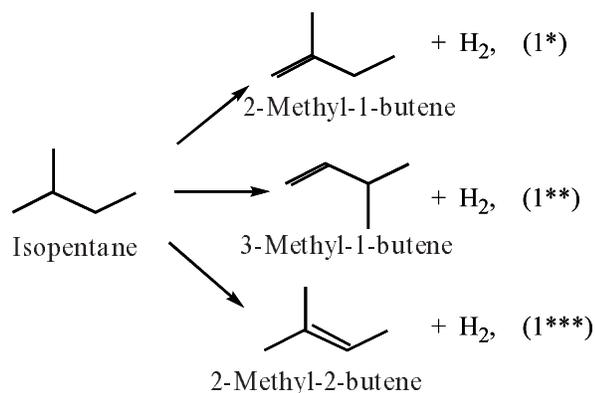
Now, we can identify the thermal effect of the corresponding reactions of 2-methybutane dehydrogenation to monoolefins as ΔH_1^*, ΔH_1^{**}, and ΔH_1^{***} and the selectivity of formation of the corresponding olefins as S_1^*, S_1^{**}, and S_1^{***}, after which we can transform the expression for the amount of heat consumed in dehydrogenation of 2-methylbutane to monoolefins as follows:

$$\Delta H_1^* \alpha_{isopentane} S_{pentene} = \Delta H_1^* \alpha_{isopentane} S_{pentene} S_1^*$$

$$+ \Delta H_1^{**} \alpha_{isopentane} S_{pentene} S_1^{**}$$

$$+ \Delta H_1^{***} \alpha_{isopentane} S_{pentene} S_1^{***}.$$

It should be noted the $S_1^* + S_1^{**} + S_1^{***} = 1$.

Thus, the final expression for calculation of the heat consumed in the course of chemical reactions proceeding in the system can be presented as follows:

$$\Delta H_{rea} = \Delta H_1^* \alpha_{isopentane} S_{pentene} S_1^* + \Delta H_1^{**} \alpha_{isopentane}$$

$$\times S_{pentene} S_1^{***} + \Delta H_1^{***} \alpha_{isopentane} S_{pentene} S_1^{***}$$

$$+ \Delta H_3 \alpha_{isopentane} S_{isoprene}. \tag{II}$$

It should be noted that, in our calculations of the thermal effect of dehydrogenation of methylbutenes to isoprene, we should take into account the thermal effect of isomerization of 2-methyl-2-butene to 2-methyl-1-butene and 3-methyl-1-butene.

Approximation of the second-order equations using the discrete values of the corresponding thermodynamic functions, performed in [8], allowed evaluation of the polynomial dependences of the enthalpies of formation and heat capacities of the system components, which were used in further calculations.

In the case of water and hydrogen, we used higher-order polynomial dependences published on the site of the National Institute of Standards and Technology (NIST, USA) [9], which are listed in Table 2.

Based on the given reaction conditions, a certain amount of water is added into the system to decrease the partial pressure of hydrocarbons and to compensate the endothermic effect of chemical reactions. Taking this fact into account, the heat capacity

Table 3. Thermodynamic characteristics of the system components in one-step dehydrogenation of 2-methybutane to isoprene at 600°C

Characteristic	Value
Enthalpy of formation, kJ mol^{-1}:	
2-methylbutane	−186.37
2-methyl-2-butene	−72.24
2-methyl-1-butene	−63.07
3-methyl-1-butene	−52.52
isoprene	58.18
Heat capacity, kJ mol^{-1} K^{-1}:	
2-methylbutane	0.262
2-methyl-2-butene	0.229
isoprene	0.209
hydrogen	0.0298
water	0.0397
Thermal effect of dehydrogenation to indicated compound, kJ mol^{-1}:	
2-methyl-2-butene	114.1
2-methyl-1-butene	123.3
3-methyl-1-butene	133.9
isoprene	244.6

of the flow at the reactor inlet is an additive quantity comprised of the heat capacities of the reactant (2-methylbutane or its mixture with methylbutenes), water, and excess hydrogen. Since the amount of the heat carrier is often taken as its molar excess with respect to the reagent, the specific heat capacity will be given hereinafter not on the gravimetric but on the molar scale. In this case, the heat capacity of the mixture at the reactor inlet, calculated per mole of 2-methylbutane introduced, can be presented by the expression:

$$(C_p)_{inlet} = (C_p)_{isopentane} + K_1(C_p)_{water} + K_2(C_p)_{hydrogen},$$

where $(C_p)_{isopentane}$, $(C_p)_{water}$, and $(C_p)_{hydrogen}$ are the molar heat capacities of 2-methylbutane, water, and hydrogen at the working temperature and pressure at the reactor inlet (kJ mol^{-1} K^{-1}), and K_1 and K_2 are the molar excesses of water and hydrogen with respect to 2-methylbutane at the reactor inlet (mole per mole of 2-methylbutane).

The heat capacity at the reactor outlet (or at the outlet from any reactor section) is constituted by the heat capacities of unchanged 2-methylbutane, reaction products (isomeric monoolefins, isoprene, and released hydrogen), and also water and hydrogen added to the system (heat carriers).

Thus, the heat capacity at the reactor outlet (or at the outlet from any reactor section) recalculated per

mole of 2-methylbutane introduced can be presented as follows:

$$(C_p)_{outlet} = (C_p)_{isopentane}\alpha_{isopentane} + (C_p)_1^*\alpha_{isopentane}$$
$$\times S_{pentene}S_1^* + (C_p)_1^{**}\alpha_{isopentane}S_{pentene}S_1^{**}$$
$$+ (C_p)_1^{***}\alpha_{isopentane}S_{pentene}S_1^{***} + (C_p)_{hydrogen}\alpha_{isopentane}$$
$$\times S_{pentene}S_1^* + (C_p)_{hydrogen}\alpha_{isopentane}S_{pentene}S_1^{**}$$
$$+ (C_p)_{hydrogen}\alpha_{isopentane}S_{pentene}S_1^{***} + (C_p)_{isoprene}$$
$$\times \alpha_{isopentane}S_{isoprene} + 2(C_p)_{hydrogen}\alpha_{isopentane}S_{isoprene}$$
$$+ K_1(C_p)_{water} + K_2(C_p)_{hydrogen}, \qquad (III)$$

where $(C_p)_{isopentane}$, $(C_p)_1^*$, $(C_p)_1^{**}$, $(C_p)_1^{***}$, $(C_p)_{isoprene}$, $(C_p)_{water}$, and $(C_p)_{hydrogen}$ are the molar heat capacities of 2-methylbutane, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, isoprene, water, and hydrogen at working temperature and pressure at the reaction outlet (kJ mol^{-1} K^{-1}) and K_1 and K_2 are the molar excesses of water and hydrogen with respect to 2-methylbutane at the reactor inlet (mole per mole of 2-methylbutane).

Since the heat capacities of isomeric monoolefins differ insignificantly (within 1%), we used not three but only one value of the heat capacity of 2-methyl-2-butene (major isomer). In this case, expression (III) can be simplified as follows:

$$(C_p)_{outlet} = (C_p)_{isopentane}\alpha_{isopentane} + (C_p)_1^{***}\alpha_{isopentane}$$
$$\times S_{pentene} + (C_p)_{hydrogen}\alpha_{isopentane}S_{pentene} + (C_p)_{isoprene}$$
$$\times \alpha_{isopentane}S_{isoprene} + 2(C_p)_{hydrogen}\alpha_{isopentane}S_{isoprene}$$
$$+ K_1(C_p)_{water} + K_2(C_p)_{hydrogen} = (C_p)_{isopentane}\alpha_{isopentane}$$
$$+ (C_p)_1^{***}\alpha_{isopentane}S_{pentene} + (C_p)_{isoprene}\alpha_{isopentane}S_{isoprene}$$
$$+ K_1(C_p)_{water} + (C_p)_{hydrogen}(\alpha_{isopentane}S_{pentene}$$
$$+ 2\alpha_{isopentane}S_{isoprene} + K_2). \qquad (IV)$$

The thermodynamic characteristics of the system components at 600°C, determined using the above equations, are listed in Table 3. As seen from these data, the reactions of dehydrogenation of 2-methylbutane to methylbutenes and to isoprene are strongly endothermic are require supply of heat into the reaction zone to maintain the process parameters.

Taking into account the actual experimental

results and the above theoretical reasoning, we simulated the one-step dehydrogenation of isopentane to isoprene in a reactor with a fixed catalyst bed. The dependences of adiabatic changes in temperature in the reactor is shown in Fig. 1 in relation to the dilution with steam and hydrogen under the following reaction conditions: temperature at the reactor inlet 600°C, starting reactant 2-methylbutane, 50% conversion of 2-methylbutane, and 85 and 15% selectivity to monoolefins and isoprene, respectively. The dependences of temperature changes on the dilution of the starting reactant with the heat carrier are described by a sixth-degree polynomial. As seen from Fig. 1, in the absence of the inert heat carriers (such as water and hydrogen), the adiabatic decrease in the temperature at the reaction outlet was 268°C. Water having higher heat capacity as compared to hydrogen is a more efficient heat carrier, which is confirmed by smaller adiabatic cooling at equal reactant : heat carrier ratio in the case of water.

It should be noted that, in dehydrogenation of 2-methylbutane using aluminum–platinum catalysts promoted with tin compounds, addition of hydrogen is necessary for reducing the active component. Under the laboratory conditions, the starting reactant was diluted with hydrogen to 1 : 1 ratio. The calculated data on the adiabatic changes in temperature in dehydrogenation of 2-methylbutane in relation to the water supply at the reactant : hydrogen molar ratio from 1 to 10 are plotted in Fig. 2 using data from Table 3. Under the given conditions (temperature at the reactor inlet 600°C, 50% conversion of 2-methylbutane, and 85 and 15% selectivity to monoolefins and isoprene, respectively), the calculated thermal effect was 845.45 kJ kg^{-1} reactant.

As seen from Table 4, under the laboratory conditions (temperature 600°C, reactant : hydrogen : water molar ratio 1 : 1 : 10, weight ratio 1 : 0.03 : 2.5), the adiabatic decrease in temperature was 89°C. The decrease in temperature within 20°C range (580–600°C is the optimal range for the reaction) can be attained only at dilution of the reactant with steam to 1 : 80 molar ratio (or 1 : 20 weight ratio). Such consumption of steam increases the production cost and decreases the process efficiency. Thus, in this case the use of an adiabatic vessel of the contact type is inappropriate.

One of the ways to solve the problem of strong adiabatic decrease in temperature in the reactor can be recycling, when after separation of isoprene the
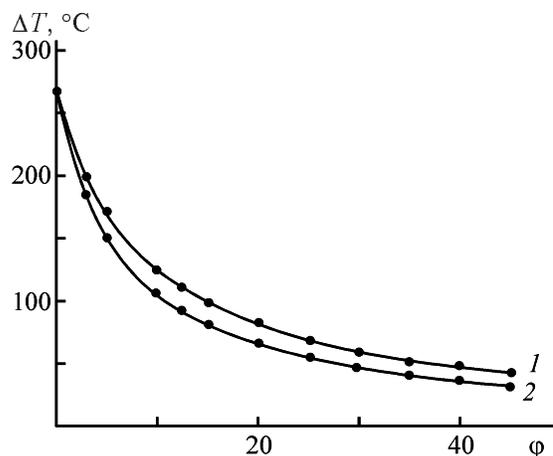

Fig. 1. Adiabatic changes in temperature in the reactor for dehydrogenation of 2-methylbutane to isoprene vs. (*1*) hydrogen : reactant and (*2*) water : reactant ratio. (ΔT) Difference between the temperatures at the reactor inlet and outlet; (φ) component ratio; the same for Fig. 2.
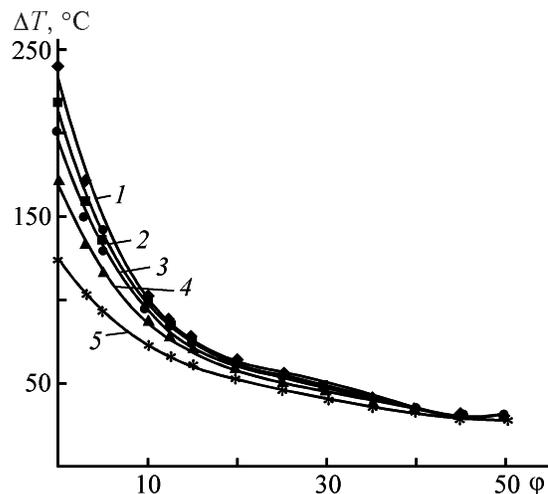
Fig. 2. Adiabatic changes in temperature in the course of 2-methylbutane dehydrogenation as function of the water supply. Reactant : hydrogen ratio: (*1*) 1 : 1, (*2*) 1 : 2, (*3*) 1 : 3, (*4*) 1 : 5, and (*5*) 1 : 10.

contact gas containing 2-methylbutane and methylbutenes is returned to the reactor. In this case, the integral thermal effect can be decreased owing to the conversion of methylbutenes. Simulation of dehydrogenation of mixtures of 2-methylbutane and methylbutenes at various selectivities to isoprene (Table 5) showed that the dilution of 2-methylbutane with methylbutenes decreases the total thermal effect and thus the difference between the temperatures at the reactor inlet and outlet.

As seen from Table 5, the selectivity of the reaction to isoprene also strongly affects the adiabatic

Table 4. Thermodynamic characteristics of 2-methylbutane dehydrogenation at various reactant : hydrogen : water ratios. Temperature 600°C, 50% conversion of 2-methylbutane, 70 and 15 wt % selectivity to methylbutenes and isoprene, respectively

Water : 2-meth-ylbutane molar ratio	Hydrogen : 2-methylbutane molar ratio									
	0 : 1		1 : 1		3 : 1		5 : 1		10 : 1	
	ΔT, °C	$\Sigma C,^*$ kJ K^{-1}	ΔT, °C	$\Sigma C,^*$ kJ K^{-1}	ΔT, °C	$\Sigma C,^*$ kJ K^{-1}	ΔT, °C	$\Sigma C,^*$ kJ K^{-1}	ΔT, °C	$\Sigma C,^*$ kJ K^{-1}
0 : 1	233	3.633	209	4.046	174	4.872	148	5.698	109	7.764
3 : 1	160	5.282	148	5.690	130	6.521	115	7.347	90	9.413
5 : 1	132	6.381	124	6.794	111	7.620	100	8.446	80	10.51
10 : 1	93	9.129	89	9.542	82	10.37	76	11.20	64	13.26
15 : 1	71	11.88	69	12.29	64	13.12	61	13.94	53	16.01
20 : 1	58	14.63	56	15.04	53	15.87	51	16.69	45	18.76
25 : 1	49	17.37	48	17.79	45	18.61	43	19.44	39	21.51
30 : 1	42	20.12	41	20.54	40	31.36	38	22.19	35	24.25
35 : 1	37	22.87	36	23.28	35	24.11	34	24.94	31	27.00
40 : 1	33	25.62	32	26.03	31	26.86	31	27.68	28	29.75
45 : 1	30	28.37	29	28.78	29	29.61	28	30.43	26	32.50
50 : 1	27	31.12	27	31.53	26	32.36	25	33.18	24	35.25

* ΣC is the reduced heat capacity of the flow at the reaction inlet.

Table 5. Thermodynamic characteristics and adiabatic changes in temperature at various selectivities to isoprene and various 2-methylbutane : methylbutenes ratios. Temperature 600°C, 1 : 1 : 10 reactant : hydrogen : water molar ratio, 50% conversion of 2-methylbutane, 30% conversion of methylbutenes, 85, x, and $85 - x$ wt % selectivities to unsaturated hydrocarbons, isoprene, and olefins, respectively

x, wt %	2-Methylbutane : methylbutenes weight ratio				
	20 : 80	40 : 60	60 : 40	80 : 20	100 : 0
	Adiabatic change in temperature, °C				
5	64	68	72	76	80
10	65	70	75	79	84
15	66	71	77	83	89
20	67	73	80	87	83
25	67	75	83	90	98
30	68	77	85	94	102
	Total thermal effect of dehydrogenation, kJ kg^{-1} reactant				
5	598.4	638.9	679.4	719.9	760.5
10	606.9	655.9	704.9	753.9	803.0
15	615.4	672.8	730.4	787.9	845.5
20	623.9	690.0	755.9	821.9	888.0
25	632.4	706.9	781.4	855.9	930.5
30	640.9	723.9	806.9	889.9	973.0

decrease in the temperature in the reactor. However, it should be noted that the data given in Table 5 were calculated on the assumption that the degree of conversion of 2-methylbutane and methylbutenes are constant and equal to 50 and 30%, respectively.

Thus, the total conversion of the mixture of 2-methylbutane and methylbutenes is 80%. At the same time, the real conversions attained in the experiments do not exceed 50%.

The experiments with catalysts that attained the

Table 6. Thermodynamic characteristics and adiabatic changes in temperature at various conversions of 2-methyl-butane and methylbutenes. Temperature 600°C, reactants : hydrogen : water molar ratio 1 : 1 : 10, 18 and 67 wt % selectivity to isoprene and olefins, respectively

Conversion, %		2-methylbutane : methylbutenes weight ratio						
isopentane	isopentenes	0 : 100	20 : 80	40 : 60	50 : 50	60 : 40	80 : 20	100 : 0
Adiabatic change in temperature, °C								
0	50	100	79	59	49	39	20	0
10	40	80	67	55	49	42	30	18
20	30	60	55	50	48	46	41	37
30	20	40	43	46	47	49	52	55
40	10	20	31	41	47	52	63	73
50	0	0	19	37	46	55	73	91
Total thermal effect of dehydrogenation, kJ kg^{-1} reactant								
0	50	929.7	743.8	557.8	464.9	371.6	185.9	0
10	40	743.8	630.0	515.9	460.0	402.0	288.1	174.2
20	30	557.8	515.9	474.1	453.1	432.2	390.3	348.7
30	20	371.9	402.0	432.2	447.2	462.3	492.4	522.6
40	10	185.9	288.1	390.3	441.4	492.4	594.6	696.8
50	0	0	174.2	348.4	435.5	522.3	696.8	871.0

Table 7. Thermodynamic characteristics and adiabatic changes in temperature at various conversions of 2-methyl-butane at 530–620°C. 2-Methylbutane : hydrogen : water molar ratio 1 : 1 : 12.5, 15 and 70 wt % selectivity to isoprene and methylbutenes, respectively

Process characteristic	2-Methylbutane conversion, %						
	10	20	30	40	50	60	70
Total thermal effect of reactions, kJ kg^{-1} reactants	12.2	24.4	36.6	48.8	61.0	73.2	85.4
Heat capacity of flow, T_{inlet} = 600°C, kJ K^{-1}:							
at reactor inlet	0.788	0.788	0.788	0.788	0.788	0.788	0.788
at reactor outlet	0.574	0.622	0.670	0.719	0.767	0.815	0.864
at indicated T_{inlet}, °C:							
530	16	32	48	64	80	96	112
560	16	31	47	63	79	94	110
580	15	31	46	62	78	93	109
600	15	31	46	62	77	93	108
620	15	31	46	61	77	92	108

steady operation mode showed that, with the supply of methylbutenes, the conversion was about 30%; in this case, the yield of isoprene reached 25–28% (based on the passed reactant), at the selectivity of about 80%. With the mixed reactants (2-methyl-butane and methylbutenes), the yield of isoprene (based on the passed reactants) increased by 2–4% as compared to the 2-methylbutane and reached 18 wt %, with the total conversion of 40–50%. Since both 2-methylbutane and methylbutenes participate in the dehydrogenation, the conversion of each component considered separately is indefinite. The calculated thermodynamic characteristics, assuming that conversions of 2-methylbutane and methyl-butenes are interrelated, are listed in Table 6. The total conversion of the reactants was taken as 50%, and the conversions of 2-methylbutane and methyl-butenes were taken as x and $50 - x$, respectively.

As seen from Table 6, the integral thermal effects of the reactions decrease owing to the dehydrogenation of methylbutenes. As a result, the difference between the temperatures at the reactor inlet and outlet decreases. However, the experimental data show that, despite an increase in the isoprene yield, with increasing content of methylbutenes in the mixture the conversion and selectivity (owing to thermodynamic factors) decrease. Taking into account this fact, it should be noted that in the case of recycling it is advisable to dilute 2-methylbutane with methylbutenes up to 80 : 20–70 : 30 ratio. In this case, the adiabatic decrease in temperature varies within the 20–73°C range depending on the conversion of 2-methylbutane and methylbutenes. The catalytic experiments performed with a mixture containing 70 wt % 2-methylbutane and 30 wt % methylbutenes showed that the content of methylbutenes in the contact gas decreased by 10–12%. Hence, if we consider that the conversion of methylbutenes is 10%, then adiabatic decrease in reactor temperature will be 63 and 52°C for the mixtures containing 2-methylbutane and methylbutenes in the 80 : 20 and 60 : 40 ratios, respectively.

One of the solutions of the problem in hand is the use of a two- or three-reactor system with intermediate heating. These reactors are filled with a catalyst. The starting reactants heated to 450–500°C are fed, along with superheated steam and hydrogen in a certain ratio, to reactor 1, where dehydrogenation proceeds at 580–600°C and the conversion of 2-methylbutane is controlled so that the adiabatic decrease in the temperature in the reactor does not exceed 20–25°C. Then the contact gas from reactor 1 is transferred into a heater, where it is heated to the reaction temperature and then is fed to reactor 2.

The thermodynamic characteristics of 2-methylbutane dehydrogenation depending on the conversion are listed in Table 7. As can be seen, a less than 25°C decrease in temperature can be attained at the conversion of about 15%. Hence, to attain the total conversion of 45–50%, the dehydrogenation should be performed using at least three reactors.

CONCLUSIONS

(1) The calculated adiabatic changes in temperature in the course of dehydrogenation of 2-methylbutane to monoolefins and then to isoprene under the set conditions show that, in the optimal reaction mode, the adiabatic decrease in the reactor temperature is 89°C. The decrease in the temperature within 20–25°C range can be attained only on dilution of the starting reactants with steam to 1 : 80 molar ratio (1 : 20 weight ratio). The consumption of such amount of steam increases the product cost and decreases the process efficiency. Thus, the use of an adiabatic vessel of the contact type is not appropriate in this case.

(2) Simulation of dehydrogenation of a mixture of 2-methylbutane and methylbutenes at various selectivity to both isoprene and methylbutenes showed that the dilution of 2-methylbutane with methylbutenes decreases the total thermal effect and correspondingly the difference in temperatures at the reactor inlet and outlet. Taking into account the real conditions of operation of the aluminum–platinum catalyst, the thermodynamic parameters of the one-step dehydrogenation were evaluated. It was found that, in dehydrogenation of a mixture containing 2-methylbutane (80%) and isopentenes (20%), the adiabatic decrease in the reactor temperature should be 63°C, and for 60 : 40 isopentane : isopentenes mixture this decrease comprises 52°C. Thus, our calculations showed that one of the solutions of the problem of a strong adiabatic decrease in the reactor temperature is recycling, when after separation of isoprene the contact gas containing significant amounts of methylbutenes is returned to the reactor.

(3) A reactor with intermediate heating of the reaction mixture was suggested as the optimal solution. The thermodynamic calculations of the isopentane dehydrogenation at varied degree of conversion showed that the adiabatic decrease in temperature within 25°C can be attained at conversion of about 15% and, thus, to attain the total conversion of 45–50%, the dehydrogenation should be performed using at least three reactors.

REFERENCES

1. Busygin, V.M., Gol'manov, Kh.Kh., Lamberov, A.A., et al., *Katal. Prom–sti.*, 2005, no. 4, p. 41.
2. Buyanov, A.V. and Pakhomov, N.A., *Kinet. Katal.*, 2001, vol. 42, no. 1, p. 72.
3. Kotel'nikov, G.R., Potapov, V.A., Buyanov, R.A., and Bushin, A.N., *Issledovanie i pazrabotka tekhnologii proizvodstva monomerov i sinteticheskikh kauchukov* (Research and Development of Technologies for Production of Monomers and Synthetic Rubbers), Moscow: TsNIITEneftekhim, 1979, p. 11.

4. Pakhomov, N.A. and Buyanov, R.A., *Zh. Prikl. Khim.*, 1997, vol. 70, no. 7, p. 1133.

5. Lyu Kam Lok, Gaidai, N.A., Kiperman, S.M., and Ho Shi Tho-ang, *Kinet. Katal.*, 1995, vol. 36, no. 4, p. 558.

6. Bol'shakov, D.A., Basner, M.E., Shmulevich, E.A., et al., *Neftekhimiya*, 1974, vol. 14, no. 2, p. 180.

7. Kirpichnikov, P.A. et al., *Ravnovesie reaktsii odnostadiinogo degidrirovaniya butana v butadien i izopentana v izopren: Khimiya i tekhnologiya monomerov dlya sinteticheskogo kauchuka* (Equilibria of the One-Step Dehydrogenation of Butane to Butadiene and Isopentane to Isoprene: Chemistry and Technology of Monomers for Synthetic Rubbers), Leningrad: Khimiya, 1981, p. 72.

8. Zhorov, Yu.N., *Termodinamika khimicheskikh protsessov* (Thermodynamics of Chemical Processes), Moscow: Khimiya, 1985.

9. http://www.nist.gov. The National Institute of Standards and Technology (NIST).