ISSN 0023-1584, Kinetics and Catalysis, 2014, Vol. 55, No. 6, pp. 705–711. © Pleiades Publishing, Ltd., 2014.
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Efficiency of Sulfonic Cation-Exchange Resins Used in *para-tert*-Butylphenol Production: A Comparison Based on the Kinetics of Transalkylation in the Phenol–*tert*-Butylphenols System

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Received January 14, 2014

Abstract—The kinetics of transalkylation in the phenol–*tert*-butylphenols system in the presence of Amberlyst 36 Dry sulfonic cation-exchange resin has been investigated at 353–403 K in the *tert*-Bu/Ar = 0.10–0.55 mol/mol range. Kinetic characteristics of the *o-tert*-butylphenol + phenol $\rightleftarrows$ *p-tert*-butylphenol + phenol (I) and 2,4-di-*tert*-butylphenol + phenol $\rightleftarrows$ 2*p-tert*-butylphenol (II) reactions have been determined. The chemical equilibrium in the presence of Amberlyst 36 Dry is reached much sooner than in the presence of KU-23 10/60, a cation-exchange resin used at present. On passing from Amberlyst 36 Dry to KU-23 10/60, the preexponential factor for reaction (I) increases by a factor of 10 and that for reaction (II) increases by a factor of 2000. Thermodynamic characteristics of reaction (I) between 353 and 523 K have been calculated from experimental data and data available from the literature. The thermodynamic characteristics of reaction (II) have been determined experimentally. The enthalpy and entropy of reaction (I) are equal to those of reaction (II). The difference between the equilibrium constants of these reactions is explained. It is recommended that Amberlyst 36 Dry, which proved more efficient than KU-23 10/60, be used in the industrial production of *p-tert*-butylphenol.

DOI: 10.1134/S0023158414060147

Consumers are imposing increasingly high requirements on products of bulk organic and petrochemical syntheses in the context of the present-day severe competition conditions. Provided that the original technologies have been explored well, there are only a few ways of improving the quality of the products without reducing the process efficiency. Such technologies include the synthesis of *para-tert*-butylphenol (PTBP) by the catalytic alkylation of phenol with isobutylene followed by transalkylation of the reaction mixture for raising the yield of the target product. The industrial-scale production of PTBP was started in 1978 at Novokuibyshevsk Petrochemical Plant (now UK "SamaraNefteOrgSintez" holding). The results of research in this field [1] had led the company in 1986 to replace the gel catalyst KU-2-8 with the macroporous sulfonic cation-exchange resin KU-23. The process is carried out under near-equilibrium conditions, with liquid isobutylene fed into the reactor.

At its refinement stage, this technology was changed to make the process more efficient. This issue is still significant, and all stages of the process are being studied in detail [1–15]. Most publications dealing with this process appeared in 1981–1990. It is in this period that the domestic PTBP synthesis technology based on phenol alkylation with isobutylene was developed and commercialized.

At the contemporary stage of technological development, a wide variety of next-generation sulfonic cation-exchange resin possessing better catalytic and mechanical properties have appeared on the market [16, 17]. However, there is no sufficient theoretical base for passing to other catalytic systems.

The purpose of this work is to find more active and more selective catalysts through kinetic and thermodynamic experiments.

At present, there is a broad assortment of ion-exchange resins, and many of them are considered as catalysts for particular processes. Amberlyst 36 Dry (A-36 Dry) is intended for phenol alkylation. Like KU-23 and KU-2-8, A-36 Dry is supplied in active, hydrogen form. KU-23 and KU-2-8 have a larger specific pore volume and a wider particle size distribution. Compared to these resins, A-36 Dry has a higher static exchange capacity (Table 1), which implies a higher sulfo group concentration. The main source of the high activity of A-36 Dry in the process considered is

Table 1. Physicochemical properties of cation cation-exchange resin

Property	KU-2-8	KU-23 10/60	Amberlyst 36 Dry
Particle size:			
– mesh range, mm	0.4–1.25	0.315–1.250	0.3–1.18
– volume fraction of working fraction, %, no less than	96	95	–
Water content, wt %	48–58	50–70	≤1.65
Specific pore volume in the H-form, cm^3/g, no less than	2.7	3.7	0.2
Specific surface area, m^2/g	–	5–25	33
Total EC, mol/cm^3 ($mg\text{-}equiv/cm^3$), no less than	4.5–4.6	4.5–4.6	≥5.40
Osmotic stability, %, no less than	96	93	–

* EC = exchange capacity.

not associated with the properties of the cation-exchange resin and has not been divulged by the manufacturer.

EXPERIMENTAL

To determine and compare catalytic activities, we used the macroporous sulfonic cation-exchange resin A-36 Dry. Kinetic data on TBP conversion over the KU-23 and KU-2-8 cation exchangers were taken from an earlier work [1].

The kinetic study of the totality of reactions occurring in the phenol–*tert*-butylphenols system was carried out by the static method in a stirred reactor. Isothermality of the process was ensured by supplying a temperature-controlled heat carrier into the reactor jacket and by continuous stirring of the reaction mixture.

It was experimentally established that the external diffusion limitations are eliminated when the rotational speed of the blade stirrer is 850 rpm or above. For this reason, in the subsequent experiments the rotational speed of the stirrer was set to be 850 rpm.

Cation-exchange resins (like all ion exchangers) swell in organic solvents [8]. The catalytic activity of sulfonic cation-exchange resins varies as they swell and their spatial structure stabilize. The preliminary swelling of cation-exchange resins in phenol at the measurement temperature for 1 h helped avoid the difficulties associated with the instability of catalyst operation at the early stages of the process.

The A-36 Dry catalyst was prepared by drying the cation-exchange resins at 110°C to constant weight within 0.01% and by washing it with a twice larger volume of phenol (whose water content was determined by GLC). The residual water content of the catalyst was 0.80 ± 0.05 wt %. Phenol to be introduced into the reaction was dried by vacuum distillation. The residual water content of phenol used in the experiments was 0.08 wt %.

The conversion rate of the reaction components was measured both in pre-prepared mixtures introduced into the reaction zone and in mixtures prepared in the reactor. The mixture components were phenol, PTBP, *ortho*-*tert*-butylphenol (OTBP), 2,4-di-*tert*-butylphenol (2,4-diTBP), and, in some experiments, 2,6-di-*tert*-butylphenol (2,6-diTBP) and 2,4,6-tri-*tert*-butylphenol (2,4,6-triTBP). At isobutylene : phenol = 0.25 and 353–383 K, 2,6-diTBP and 2,4,6-triTBP, which are sterically hindered compounds, turned completely into mono-TBP and 2,4-diTBP at a high rate (which was one order higher than the rate of the other reactions). The initial point of a kinetic experiment was taken to be the instant the isobutylene supply was shut off or the introduction of the artificial mixture. Irrespective of the procedure used, the results of the experiment were absolutely the same. Reaction mixture samples did not need to be pretreated before being analyzed.

Kinetic experiments were performed with the same catalyst batch, which was 8–12% of the weight of the reaction mixture. The density of the reaction mixture was determined using the chemical modeling program HYSYS.Process (version v2.2).

The reaction mixture was analyzed by GLC on two chromatographs: Tsvet-800 (Tsvet Co., Russia, 3-m-long packed column, Chromaton N + 3% OV-17 + 1% NPGS stationary phase, injection port temperature of 623 K, oven temperature of 553 K, helium as the carrier gas, inlet pressure of 3 atm) and Kristall-2000 (Khromatek Co., Russia, 50 m × 0.25 mm quartz capillary column, grafted SE-50 stationary phase, injection port temperature of 543 K, detector temper-

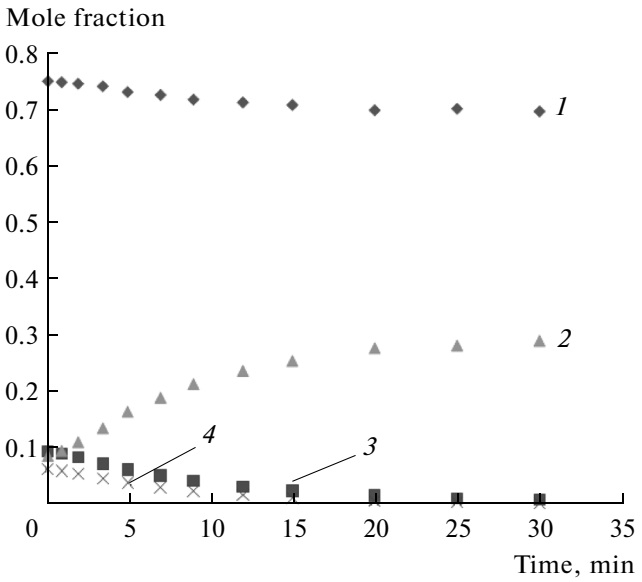

Fig. 1. Results of a typical kinetic experiment: (*1*) phenol, (*2*) PTBP, (*3*) OTBP, and (*4*) 2,4-diTBP.

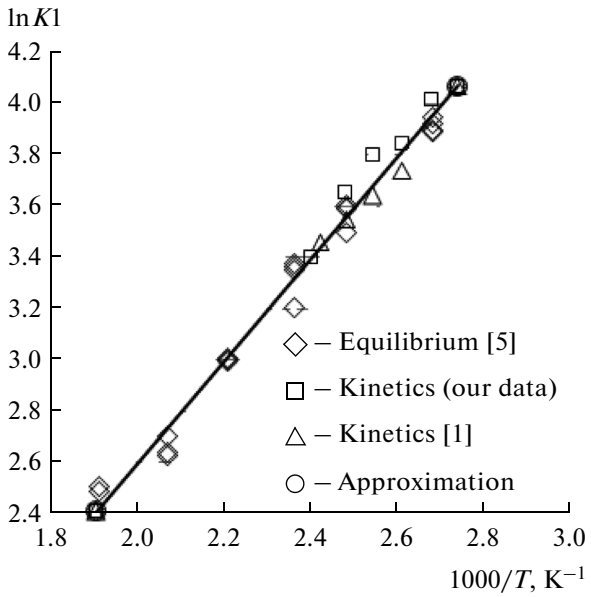

Fig. 2. Results of investigation of reaction (I) equilibrium.

ature of 473 K, helium as the carrier gas, inlet pressure of 3 atm, 1 : 15 flow division).

RESULTS AND DISCUSSION

The kinetic experiments were performed at 353, 373, 383, 393, and 403 K. The molar ratio of *tert*-butyl groups to aromatic nuclei was varied in the 0.10–0.55 range, as in the real industrial processes. Figure 1 presents typical experimental data illustrating the time variation of the concentration of each component and the entry of the reaction into the thermodynamically controlled area.

Between 373 and 403 K at all reactant ratios, the system reached the equilibrium and contained only four components: phenol, OTBP, PTBP, and 2,4-diTBP. The rank of the stoichiometric matrix for this reaction is 2. Therefore, for describing the equilibrium in this system (as a whole), its is necessary and sufficient to know equilibrium constants for two independent reactions. We chose the following ones:

$$\text{OTBP} + \text{phenol} \rightleftarrows \text{PTBP} + \text{phenol}, \quad \text{(I)}$$

$$\text{2,4-diTBP} + \text{phenol} \rightleftarrows \text{PTBP} + \text{PTBP}. \quad \text{(II)}$$

The amounts of experimental data available on these reactions are different. The liquid-phase equilibrium in reaction (I) has been comprehensively studied (Table 2). The information that was provided by the task-oriented investigation of this equilibrium and was systematized by Nesterov [5], the data calculated by us in a similar study, and the results of the kinetic experiment carried out by Rempel [1] are in good agreement (Fig. 2). The simultaneous processing of all of the data (Table 2) yielded linear approximation coefficients (Table 3), which were used to calculate the enthalpy and entropy of the reaction.

The enthalpy and entropy of the liquid-phase reactions (I) and (II) are pairwise equal within the error of their determination (Table 3). The equilibrium constants of the reactions, which are more sensitive thermodynamic characteristics, differ significantly (Table 3, Fig. 3). The data plotted in Fig. 3 suggest that difference disappears entirely on passing from the liquid-phase reactions to the gas-phase ones. (The calculation was carried out under the assumption that Raoult's law is valid using vapor pressures from [15, pp. 336–338].) Thus, the fact that the K_2 values are larger than the K_1 values is due to intermolecular, not intramolecular factors. This information is significant for predicting the thermodynamic properties of *tert*-alkylphenols.

The results of the study of the equilibrium (Table 3) provided a basis for processing the kinetic data obtained by us for the following system of reactions:

$$\text{OTBP} + \text{phenol} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{PTBP} + \text{phenol}, \quad (1; -1)$$

$$\text{2,4-diTBP} + \text{phenol} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{PTBP} + \text{PTBP}, \quad (2; -2)$$

$$\text{2,4-diTBP} + \text{phenol} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \text{OTBP} + \text{OTBP}, \quad (3; -3)$$

$$\text{2,4-diTBP} + \text{phenol} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \text{PTBP} + \text{OTBP}, \quad (4; -4)$$

$$\text{2,4-diTBP} + \text{OTBP} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \text{2,4-diTBP} + \text{PTBP}. \quad (5; -5)$$

Table 2. Chemical equilibrium data for reactions (I) and (II)

T, K	n*	m*	K_i	Source	T, K	n*	m*	K_i	Source
ortho-tert-Butylphenol ⇄ *para-tert*-Butylphenol (I)									
353	12	2	71.4 ± 1.1	[5] (equilibrium)	403	90	18	34.9	[1] (kinetics)
	9	1	69.3 ± 2.9	″	413	30	6	31.9	″
373	15	3	55.7 ± 3.1	This work	417	3	1	30.1 ± 0.5	This work
	19	3	49.1 ± 0.5	[5] (equilibrium)	423	57	8	29.0 ± 0.4	[5] (equilibrium)
	3	1	49.3 ± 1.1	″		35	3	28.6 ± 0.5	″
	16	3	51.9 ± 1.5	″		15	3	29.3±1.0	″
	18	2	50.6 ± 1.9	″		31	43	24.7 ± 0.7	″
383	14	3	46.8 ± 2.3	This work	453	40	6	20.1 ± 0.2	″
	25	5	42.2	[1] (kinetics)		18	3	20.2 ± 0.3	″
393	7	1	44.9 ± 1.1	This work		10	2	20.3 ± 0.9	″
	50	10	38.3	[1] (kinetics)	483	46	7	13.9 ± 0.5	″
403	25	3	38.8 ± 0.4	This work		31	5	14.1 ± 0.8	″
	44	6	36.3 ± 0.3	[5] (equilibrium)		9	2	15.0 ± 0.6	″
	19	3	36.3 ± 0.4	″	523	29	5	12.3 ± 0.3	″
	11	2	36.8 ± 0.4	″		16	3	12.1 ± 0.7	″
	19	2	33.1 ± 0.9	″					
2,4-diTBP + phenol ⇄ PTBP+ PTBP (II)									
373	13	3	88.7 ± 5.2	This work	403	27	3	59.0 ± 1.1	This work
383	14	3	73.3 ± 3.4	″	417	2	1	46.7	″
393	8	1	62.5 ± 5.2	″					″

* n is the number of successful measurements of the equilibrium constant; m is the number of significantly different series of determinations of K_1 and K_2.

Table 3. Thermodynamic characteristics of liquid-phase reactions (I) and (II)

Reaction	Coefficients of the equation $\ln K = a + 1000b/T$		T_{mean}, K	$\Delta_r H^0$ (T_{mean}), kJ/mol	$\Delta_r S^0$ (T_{mean}), J mol^{-1} K^{-1}
	a	b			
(I)	−1.3704	1.9865	417	−16.5 ± 0.8	−11.4 ± 1.8
(II)	−1.3380	2.1647	394	−18.0 ± 1.0	−11.1 ± 2.5

T_{mean} is the mean experimental temperature, $\Delta_r H^0$ is the enthalpy of reaction, and $\Delta_r S^0$ is the entropy of reaction.

The kinetic model of the process is given by the following system of differential equations for the key components chosen by us—OTBP and 2,4-diTBP:

$$d[\text{OTBP}]/d\tau = k_{-1}[\text{PTBP}][\text{phenol}] - k_1[\text{OTBP}][\text{phenol}] + 2k_3[\text{2,4-diTBP}][\text{phenol}] - k_{-3}[\text{OTBP}]_2 + k_4[\text{2,4-diTBP}][\text{phenol}] - k_{-4}[\text{OTBP}][\text{PTBP}] - k_5[\text{2,4-diTBP}][\text{OTBP}] + k_{-5}[\text{2,4-diTBP}][\text{PTBP}],$$

$$d[\text{2,4-diTBP}]/d\tau = k_{-2}[\text{PTBP}]^2 - k_2[\text{2,4-diTBP}][\text{phenol}] + k_{-3}[\text{OTBP}]^2 - k_3[\text{2,4-diTBP}][\text{phenol}] + k_{-4}[\text{OTBP}][\text{PTBP}] - k_4[\text{2,4-diTBP}][\text{phenol}].$$

The experimental conditions and the data array used in the calculation of mean rate constants are listed in Table 4.

The effective rate constants of individual reactions were calculated by the differential method from the entire experimental data array and from the equilibrium constants of the reactions (Table 3). The optimization criterion was

$$\Sigma_n\left(\left(\frac{dc_i}{dt}\right)_{exp} - \left(\frac{dc_i}{dt}\right)_{calc}\right)^2 = 0,$$

where n is the number of measurements.

It was established that, in the isobutylene : phenol = 0.10–0.55 mol/mol range, only the rate constants of reversible reactions (I) and (II) are significant. The k_1 and k_2 obtained by us for the A-36 Dry sulfonic cation-exchange resin are presented in Table 4, where they are compared with the constants obtained by Rempel [1] for the same reactions catalyzed by KU-2-8 and KU-23 10/60.

With A-36 Dry, the rate constants of these reactions are larger even at lower temperatures. Thus, this catalyst makes it possible to reach the equilibrium much sooner. The calculation of activation parameters for reactions (I) and (II) (Table 5) confirmed this finding.

Rempel [1] put forward the hypothesis that the activation energy E_a of each of these reactions is independent of the cation-exchange resin brand and the effect of the specific surface area of the catalyst can have an effect only on the preexponential factor $k_{i,0}$. Here, the mechanism of catalysis should not change from one catalyst to another and the process should be controlled by external kinetics. These conditions were satisfied in our study, enabling us to use this hypothesis in the processing of experimental data.

The results presented in Table 5 demonstrate the following:

(1) The activation energies of reactions (I) and (II) occurring over A-36 Dry are practically equal to the E_a values calculated by simultaneous processing (within the above hypothesis) of the entire data array for the three catalysts (A-36 Dry, KU-2-8, and KU-23 10/60).

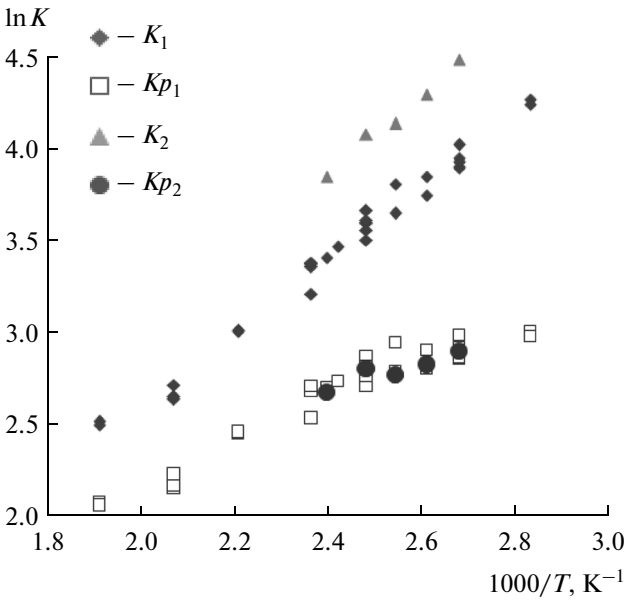

Fig. 3. Equilibrium constants for reactions (I) and (II) in the liquid phase (*Ki*) and in the gas phase (*Kpi*).

(2) The preexponential factors for the two reactions are different and decrease in the following order: A-36 Dry > KU-23 10/60 > KU-2-8.

The data of this study suggest that the sulfonic cation-exchange resin KU-23 10/60 is less active than Amberlyst 36 Dry. In addition, A-36 Dry is characterized by a narrower particle size distribution (Table 1), according to the manufacturer's data, and is thermally more stable (its upper operating limit is 150°C against 130°C for > KU-23 10/60). The deactivation of the sulfonic cation-exchange resin is mainly due to the thermally induced washout of sulfo groups from their surface and also due to mechanical destruction. Based on the experience in the industrial operation of KU-23 10/60 resin and on the temperature range in which it is efficient (80–130°C), it can be expected that Amberlyst 36 Dry will have a longer service life.

Replacing the KU-23 10/60 cation cation-exchange resin with Amberlyst 36 Dry in the industrial process will increase the product yield per unit volume of the reaction zone. In addition, changing to A-36 Dry will reduce the consumption of washing phenol in the pre-operation treatment of the cation cation-exchange resin, since the moisture content of as-received A-36 Dry does not exceed 1.65 wt %, while that of KU-23 10/60 is 50–70 wt %.

Thus, based on experimental data and information available from the literature, we determined thermodynamic characteristics of the independent reactions describing the equilibrium in the system consisting of phenol, *p-tert*-butylphenol, *o-tert*-butylphenol, and 2,4-di-*tert*-butylphenol.

The kinetics of transalkylation of the *tert*-butylphenols in the presence of the sulfonic cation-exchange

Table 4. Results of the kinetic study using the mean values of rate constants at different temperatures

Sulfonic cation-exchange resin	T, K	Experimental conditions*	$k_1 \times 100$**	$k_2 \times 100$**
			$L^2\ mol^{-1}\ kg^{-1}\ min^{-1}$	
Amberlyst 36 Dry (this work)	353	*tert*-Bu/Ar = 0.25–0.33, cat = 9–10.5%, $n = 47$, $m = 3$	5.358 ± 0.053	6.731 ± 0.118
	373	*tert*-Bu/Ar = 0.27–0.34, cat = 9–9.7%, $n = 41$, $m = 3$	15.405 ± 0.151	14.658 ± 0.147
	383	*tert*-Bu/Ar = 0.1–0.55, cat = 7.7–12.4%, $n = 80$, $m = 8$	28.955 ± 0.251	30.013 ± 0.176
	393	*tert*-Bu/Ar = 0.26–0.32, cat= 8.2%, $n = 10$, $m = 1$	40.604 ± 0.732	30.745 ± 0.535
	403	*tert*-Bu/Ar = 0.39–0.54, cat = 8.5–9.1%, $n = 49$, $m = 3$	69.090 ± 0.053	62.156 ± 0.051
KU-2-8 [1]	393	*tert*-Bu/Ar = 0.5, $n = 75$, $m = 3$	1.470 ± 0.018	0.009 ± 0.000
	403	*tert*-Bu/Ar = 0.25–0.7, $n = 225$, $m = 9$	3.738 ± 0.036	0.015 ± 0.000
	413	*tert*-Bu/Ar = 0.5, $n = 75$, $m = 3$	8.700 ± 0.060	0.029 ± 0.000
KU-23 10/60 [1]	383	*tert*-Bu/Ar = 0.46–0.51, $n = 75$, $m = 3$	2.034 ± 0.024	0.018 ± 0.000
	393	*tert*-Bu/Ar = 0.5, $n = 75$, $m = 3$	5.424 ± 0.048	0.032 ± 0.000
	403	*tert*-Bu/Ar = 0.5, $n = 75$, $m = 3$	13.860 ± 0.120	0.055 ± 0.000

* *tert*-Bu/Ar is the molar ratio of *tert*-butyl groups to phenol nuclei in the reaction mixture, Cat is the amount of catalyst per unit weight of the reaction mixture, n is the number of measurements, and m is the number of experimental series.

** Mean value of the rate constant at each temperature point examined.

Table 5. Activation parameters of reactions (I) and (II)

Catalyst	Reaction (I)		Reaction (II)	
	E_a, kJ/mol	$\ln k_{i,0}$	E_a, kJ/mol	$\ln k_{i,0}$
Amberlyst 36 Dry (separate)	60.9 ± 5.0	17.8 ± 1.6	53.4 ± 6.2	15.4 ± 1.8
Amberlyst 36 Dry	64.4	18.9	51.8	15.5
KU-23 10/60		16.8		7.8
KU-2-8		15.8		6.6

resin Amberlyst 36 Dry was studied. It was demonstrated that replacing KU-23 10/60 with Amberlyst 36 Dry, a more efficient catalyst, would increase the target product yield per unit volume of the reaction zone, extend the service life of the catalyst, widen the allowable process temperature range by lowering the initial synthesis temperature and raising the final one, and reduce the consumption of washing phenol at the cation-exchange resin pretreatment stage.

It was observed experimentally that the equilibrium in the system involving Amberlyst 36 Dry is established much sooner than in the case of KU-23 10/60 or KU-2-8. Under the assumption that the activation energy of the reaction is invariable, it was demonstrated that, on passing from Amberlyst 36 Dry to KU-2-8 and KU-23 10/60, the preexponential factor of reaction (I) increases by a factor of 20 and 10,

respectively, and that of reaction (II) increases by a factor of 7000 and 2000.

ACKNOWLEDGMENTS

This study was supported by the Ministry of Education and Science of the Russian Federation in the framework of the base part of the governmental assignment for Samara State Technical University (project code 1708).

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Translated by D. Zvukov