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E.S. Mammadova^a, *Z.Ch. Salaeva*^a, *A.E. Huseinova*^b, *G.A. Mammadaliev*^a**SYNTHESIS AND APPLICATION OF ALKYLPHENOLS OBTAINED BY ALKYLATION OF PHENOL WITH C₈–C₁₀ α-OLEFINS**^a Open-Joint-Stock Company «Olefins Scientific-Research and Production Center», Baku, Azerbaijan^b Sumgait State University, Sumgait, Azerbaijan

The paper reports the results of experiments on the development of production of alkylphenols using the method of thermal alkylation of phenol with α-olefins. The influence of technological parameters, such as temperature, pressure, reaction time and molar ratio of reagents, was studied. An increase in the reaction temperature and molar ratio of phenol:olefin positively affects the degree of conversion of olefins, which reaches a maximum value of 85% at 425°C and molar ratio of phenol:olefin of 5:1. However, an increase in the reaction temperature higher than 400°C negatively affects the selectivity of the process for «extremely substituted» alkylphenols, which decreases from 97% to 76% at 400°C and 425°C, respectively. The optimum conditions of the process were found as follows: the reaction temperature of 400°C, the pressure of 6.0 MPa, the molar ratio of phenol:olefins=4:1 and the reaction time of 1 h. Under these conditions, the degree of conversion of olefins and the selectivity with respect to monoalkylphenol are equal to 50% and 90%, respectively. The possibility of full isomerization of alkylphenols ethers into relevant alkylphenols on the catalyst KU-2 was shown. Prepared alkylphenols were tested as a basis for the production of surfactants. Thermal alkylphenols were compared with acidic samples of alkylphenols. It was shown that alkylphenols prepared by thermal alkylation process allow producing surfactants, which exhibit high surface-active properties with reference to the interfacial tension of solutions «surfactants–kerosene». Based on the obtained results, the flowsheet of the thermal alkylation process of phenol with α-olefins was proposed.

Keywords: alkylation, alkylphenols, α-olefins, isomerization, optimal conditions, manufacturing scheme, process.

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Introduction

Synthetic alkylphenols are important semi-products in petrochemical industry and industrial organic synthesis. Their main bulk is consumed in the synthesis of nonionic surfactants. The use of alkylphenylpolyglycolic ethers in oil industry is a large-tonnage production for oil recovery enhancement through its flooding. Although oxyethylated normal alcohols are used for the same purposes, the cost and simplicity of production of alkylphenylpolyglycolic ethers as well as the availability of raw material represent great advantages over alcohols.

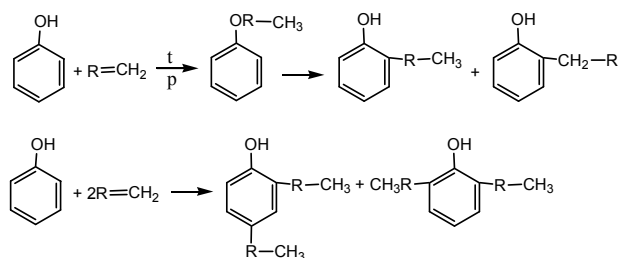
Alkylphenols are widely used in the production of oil-soluble polymers for paint-and-varnish industry. As bactericide and disinfecting agents, alkylphenols sufficiently surpass phenols, cresols, and

so on. Alkylphenols are also used as antioxidant additives to polymers and lubricating oils [1–4].

As it is known, the catalysts used for alkylation of phenol with olefins are mineral and organic acids, haloids of metals, amorphous and crystalline aluminosilicates, different phenolates, and sulfocationites (KU-2) [5]. Although alkylphenols can be obtained using some of these catalysts to obtain targeted ortho-isomer, the formation of phenol-containing wastewaters make these processes undesirable for application. Other catalysts, aluminosilicates, zeolites and KU-2, do not exhibit sufficient selective action towards the formation of ortho-isomer and lose their catalytic activity after some time [6,7]. Moreover, when using some catalysts together with monoalkylphenol, the polyalkylphenols, which have not been widely used,

are formed in small quantities.

This paper deals with the development of thermal alkylation process of phenol with linear α -olefin fraction C_8-C_{10} . The reaction proceeds according to the following scheme:



Experimental, results and discussion

Phenol (GOST 236-68, premium grade) and α -olefins C_8-C_{10} produced by high-temperature oligomerization of ethylene in the presence of organometallic catalyst [8–10] were used as raw materials.

Alkylation process was investigated by means of continuously operating installation (Fig. 1).

Phenols and olefins in a given molar ratio were heated up to 220°C in a heater (3) and passed to a hollow reactor (4), where the necessary reaction temperature and pressure were maintained. After that, the reaction products were supplied to a separator (5) and further to the system of rectification columns (6,7,8).

The reaction products were analyzed using an LKhM-8MD chromatograph (model 5) equipped with a flame ionization detector (carrier-gas was helium, carrier-gas velocity was 40 mL/min and column temperature was 50–100°C). Cellite 545 with a stationary phase benton 34+didecyl phthalate (1:1)

was used as a sorbent.

To determine the optimum ratio of phenol:olefin, a number of experiments were carried out at different temperatures and the results are shown in Fig. 2.

The highest conversion (85 wt.%) was observed at 425°C and molar ratio of 5:1.

However, an increase in the reaction temperature higher than 400°C negatively affects the selectivity of the process for «extremely substituted» alkylphenols, which decreases from 97% (at 400°C) to 76% (at 425°C) (Fig. 3).

The formation of considerable quantities of low-molecular alkylphenols is also observed, which causes the destruction of olefins under such conditions.

Pressure is an important factor in thermal alkylation of phenol. Figure 4 shows the effect of pressure on the alkylation at different reaction duration.

To achieve a maximum conversion of olefins at sufficiently high selectivity towards «extremely substituted» alkylphenols, the pressure of 50–70 atm must be kept in the system at the reaction time of 60 min. A further increase in the reaction time causes an increase in the content of isomers with «internal» substitution in alkylates.

Summarizing the obtained data, it must be noted that the reaction of thermal alkylation of phenol with α -olefins proceeds in the range of critical temperatures and pressures for phenol ($T_{cr}=419^\circ\text{C}$ and $P_{cr}=60$ atm). In compliance with the conditions of the reaction, the selectivity with respect to «extremely substituted» alkylphenols reaches about 93–95%.

Based on the experimental data (Table 1), the optimum conditions of alkylation process were determined as follows: temperature of about 400°C,

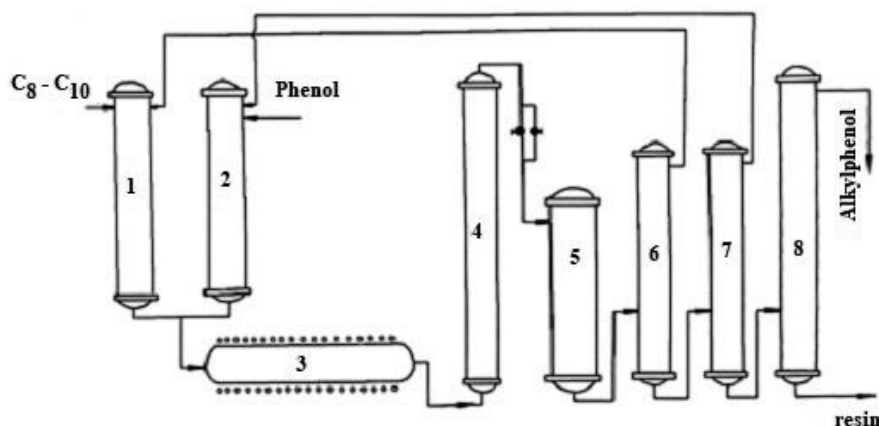


Fig. 1. Installation diagram: 1 – olefin measurer; 2 – phenol measurer; 3 – heater; 4 – reactor; 5 – separator; 6, 7, 8 – rectification columns

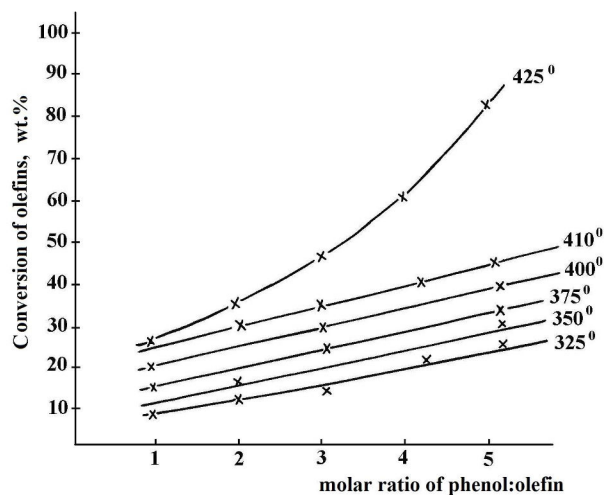


Fig. 2. Conversion of olefins as a function of molar phenol:olefin ratio at different temperatures for alkylation of phenol with olefins

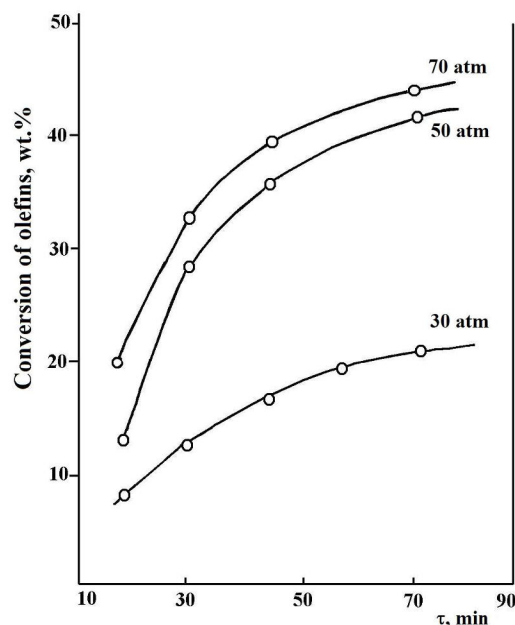


Fig. 4. The influence of pressure on the conversion of olefins

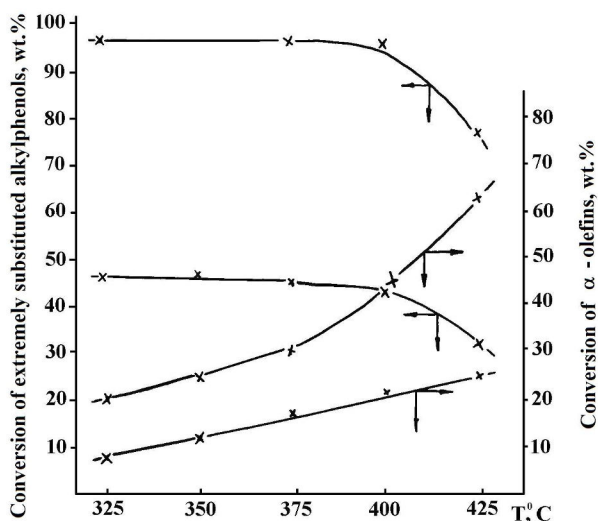


Fig. 3. Effects of temperature on the conversion of «extremely substituted» alkylphenols and the conversion of α -olefins at a molar ratio of phenol:olefin=5:1

pressure of 60 atm, molar ratio of phenols:olefins=4:1, reaction time of 1 h and density of reaction mixture 0.28–0.3 g/cm³. The best-achieved results are as follows: the conversion of olefins equals to about 50%, the selectivity with respect to monoalkylphenol is 90–96% and their yield is 45%.

We also observed the formation of alkylphenols ethers which can be easily isomerized (for 90%) into relevant alkylphenols on the catalyst KU-2 at 60°C.

The life time of the catalyst KU-2 under these conditions is not less than 1000 hours, but the spent

catalyst cannot be regenerated.

It is well known that one of the main directions of application of these alkylphenols is the production of surfactants. In case of the synthesis of surfactant based on alkylphenols, it was determined that the degree of its biodegradation is closely connected with the structure of alkylphenols in its composition. Low-soluble surfactants are obtained based on ortho-secondary alkylphenols, whereas water-soluble surfactants are obtained using highly-branched para-alkylphenols. It was also found that surfactants based on alkyaromatic compounds with linear structure, unlike their branched isomers, are characterized by high biodegradability [6–7,11].

The targeted fractions of alkylphenols were separated from the synthesized products as an initial raw material for the production of nonionic surfactants. Table 2 shows the results of comparative tests of the use of thermal alkylphenol and acidic samples of alkylphenols in the production of nonionic surfactants. One can see that nonionic surfactants which exhibit high surface-active properties with respect to the interfacial tension of solutions surfactants–kerosene can be produced based on alkylphenols and using thermal alkylation.

Conclusions

We developed the process of the synthesis of alkylphenols by alkylation of phenol with C₈–C₁₀ α -olefins and selected the optimal synthesis conditions as follows: the temperature of 400°C, the pressure of 60 atm, the phenol:olefin molar ratio of 4:1, and the reaction time of 1 h. Under these

Table 1

**Results of thermal alkylation of phenol with α -olefins C_8-C_{10} by using a flow-type installation
(the reaction time was 1 h)**

T °C	Conditions of experiments			Conversion of olefins, %	Selectivity with respect to monoalkyl-phenol, %	Yield of monoalkylphenols, %	Total yield of alkylphenols, %	Total yield of ethers, %
	Pressure, atm	Phenol:olefin	Density, g/cm ³					
375	30	1:1		7.2	93.4	5.8	5.9	0.30
375								
375								
375								
400	30	2:1	0.35	13.5	91.2	12.3	12.65	0.85
400	40	3:1		18.6	94.8	17.6	18.10	0.50
400	50	4:1		42.5	96.7	41.1	41.65	0.85
400	60	2:1		14.3	92.4	13.2	13.50	0.80
400	50	3:1		32.5	95.4	31.0	31.42	1.08
400	60	4:1		46.7	95.8	44.8	45.80	0.90
410	30	2:1		15.7	89.5	14.0	14.65	1.05
410	40	3:1		34.8	92.1	32.1	33.10	1.70
410	50	4:1	43.5	93.8	40.8	41.90	1.60	
410	60	3:1	25.8	90.5	23.4	24.30	1.50	
410	60	4:1	49.9	95.6	47.8	48.70	1.20	
410	50	3:1	38.7	96.4	37.3	38.00	0.70	
420	30	4:1	0.30	50.2	91.2	45.8	46.80	3.40
420	40	3:1		39.5	90.2	35.7	36.70	2.80
420	50	3:1		42.4	88.3	37.4	38.80	3.60
420	60	3:1		44.5	83.5	39.9	41.20	3.30
420	50	3:1		44.7	88.6	39.7	41.20	3.50
420	50	3:1						

Table 2

Characteristics of oxyethylated alkylphenols prepared by different methods

Name of alkylphenols based on α -olefins C_8-C_{10}	Molar mass of alkylphenols (calculated by hydroxyl number of alkylphenol)	Number of connected moles of ethylene oxide	Characteristics of oxyethylates				
			Content of oxyethylene, wt. %	Content of polyethylene glycol, wt. %	Freezing point, °C	Cloud point of 1% surfactant, wt. %	Interfacial tension on kerosene 0,05% surfactant
Alkylphenols of thermal alkylation	238	11.8	68.0	4.3	19,3	68–69	4.60
			15.3	73.7	5.2	20,5	90–90.5
Alkylphenols obtained by catalytic alkylation on KU-2	224	12.1	70.8	3.8	–	68–71	3.96
			15.0	74.9	4.2	22,5	89–92

conditions the olefin conversion reaches 50%, the selectivity towards monoalkylphenol is 90–96% and their yield is 45–46%. It should be noted that the obtained alkylphenols mainly consist of ortho-isomers (about 70%) which are highly biodegradable. The main advantages of thermal alkylation over the catalytic one are as follows: a high selectivity of the process, the lack of reaction by-products, the simplicity of technological design and the absence of an expensive catalyst KU-2.

The flowsheet of the synthesis of alkylphenols was developed by using thermal alkylation of phenol with α -olefins. The process includes the following stages: thermal alkylation of phenol, throttling the reaction mixture, isolation of alkylphenols and catalytic isomerization of ether and alkylphenols.

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СИНТЕЗ І ВИКОРИСТАННЯ АЛКІЛФЕНОЛІВ, ОДЕРЖАНИХ АЛКІЛУВАННЯМ ФЕНОЛУ C_8-C_{10} α -ОЛЕФІНАМИ

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У статті викладені результати досліджень стосовно розробки виробництва алкілфенолів з використанням методу термічного алкілування фенолу α -олефінами. Вивчено вплив технологічних параметрів, таких як температура, тиск, тривалість реакції і молярне співвідношення реагентів. Зростання температури і молярного співвідношення фенол:олефін позитивно впливає на ступінь конверсії олефінів, що досягає максимального значення 85% при 425°C і молярному співвідношенні фенол:олефін, рівному 5:1. Однак, збільшення реакційної температури вище, ніж 400°C негативно відбивається на селективності процесу для «екстремально заміщених» алкілфенолів, яка знижується від 97% до 76% при 400°C і 425°C, відповідно. Визначені наступні оптимальні умови процесу: реакційна температура 400°C, тиск 6 МПа, молярне співвідношення фенол:олефін=4:1 та тривалість реакції 1 год. За таких умов ступінь конверсії олефінів та селективність стосовно моноалкілфенолу становлять 50% та 90%, відповідно. Показана можливість повної ізомеризації алкілфенольних етерів у відповідні алкілфеноли на каталізаторі KU-2. Виготовлені алкілфеноли були протестовані як основа для виробництва поверхнево-активних речовин. Термічні алкілфеноли були порівняні з кислими зразками алкілфенолів. Показано, що алкілфеноли, виготовлені шляхом процесу термічного алкілування, дозволяють отримувати іонногенні поверхнево-активні речовини, що проявляють вищу

поверхневу активність стосовно міжфазного натягу розчинів «поверхнево-активна речовина – газ». На основі отриманих результатів розроблена технологічна схема процесу термічного алкілування фенолу α -олефінами.

Ключові слова: алкілування; алкілфеноли; α -олефіни; ізомеризація; оптимальні умови; технологічна схема; процес.

SYNTHESIS AND APPLICATION OF ALKYLPHENOLS OBTAINED BY ALKYLATION OF PHENOL WITH C_8-C_{10} α -OLEFINS

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