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Abstract

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SULFURIC-ACID ALKYLATION OF TOLUENE WITH C_{10} OLEFINS

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In the production of the most widespread group of synthetic detergents—alkylarylsulfonates—products of the alkylation of benzene with olefins having from 10 to 15 carbon atoms are usually employed.

However, in connection with the increasing consumption of benzene in various chemical syntheses, it becomes necessary to study the possibilities of using aromatic hydrocarbons other than benzene, in particular toluene. In the literature ([1,3–7]) there are isolated suggestions concerning the expediency of using toluene for obtaining alkylarylsulfonates; however, studies on the influence of various factors on the intensity of the reaction of alkylation of toluene with C_{10} olefins in the presence of sulfuric acid have not been published.

It has recently been shown ([8]) that the process of phosphoric-acid polymerization of amylenes contained in the C_5 fraction of thermal-cracking products offers great possibilities for obtaining high-molecular olefins, predominantly C_{10}, suitable for the production of synthetic detergents. In this connection, in carrying out the present work, the reaction of alkylation of toluene with products of polymerization of the pentane-amylene fraction in the presence of sulfuric acid was studied.

For the experiments, toluene was taken with b.p. 109.5–111°, ρ_4^{20} 0.8655, n_D^{20} 1.4956, bromine number 0, and a fraction of amylene dimers 125–175°, isolated from a broad fraction of amylene polymers and having the following properties: ρ_4^{20} 0.7663, n_D^{20} 1.4354, M 134, and bromine number 120, which corresponds to an unsaturated-hydrocarbon content of 100 wt. %.

Chemically pure sulfuric acid was used as the catalyst.

The alkylation reaction was carried out in a laboratory glass reactor, consisting of a cylinder with a spherical bottom, of 1 l capacity, equipped with a glass stirrer, a mercury seal, a thermometer, a reflux condenser, and a dropping funnel for feeding sulfuric acid. The reactor was placed in a bath equipped with a thermometer and a stirrer for intensive mixing of the cooling liquid. In carrying out an experiment, a mixture of toluene and the olefin fraction in a previously specified ratio was charged into the reactor, and then, with stirring at a rate ensuring constancy of the temperature, acid was introduced. Owing to the intensive removal of the heat of reaction, the time of addition usually amounted to 0.5 min. After introduction of the acid, the reaction mixture was stirred for the specified reaction time, allowed to settle, and the hydrocarbon layer was separated from the acid, alkalized with a 5% aqueous solution of caustic soda, washed with distilled water, dried over calcium chloride, and distilled with separation of unreacted toluene, olefin fraction, and alkyl product—the fraction above 175°. Subsequently the alkyl product was distilled at a residual pressure of 10-15 mm on a laboratory column.

with 20 theoretical plates into the fractions 175-220° and 220-300° (the target fraction) and the residue above 300°.

Numerous experiments were carried out to determine the effect on the reaction of alkylating toluene with the fraction of amylene dimers having b.p. 125-175° of the following factors: the concentration of the initial acid, the time and temperature of the reaction, the molar ratio of olefins to toluene, and the ratio of acid to hydrocarbons.

When the concentration of the initial acid was varied from 85 to 100 wt. % as monohydrate, at a temperature of 10°, a reaction time of 60 min., a molar ratio —

Table 1

Effect of temperature on the yield and properties of alkyl products. Conditions: concentration of the initial acid 96 wt. %, reaction time 60 min., volume ratio of acid to hydrocarbons 0.12, molar ratio of olefins to toluene 1 : 7

Experiment No.	Temperature, °C	Yield of alkyl product, wt. % of olefins taken	Alkyl product (fraction above 175°): ρ_4^{20}	Alkyl product (fraction above 175°): n_D^{20}	Alkyl product (fraction above 175°): bromine number	Alkyl product (fraction above 175°): fractional composition, wt. %, 175–220°	Alkyl product (fraction above 175°): fractional composition, wt. %, 220–300°	Alkyl product (fraction above 175°): fractional composition, wt. %, residue above 300°	Properties of fractions: 175–220°C, ρ_4^{20}	Properties of fractions: 175–220°C, n_D^{20}	Properties of fractions: 220–300°C, ρ_4^{20}	Properties of fractions: 220–300°C, n_D^{20}
26	−10	131,5	0,8730	1,4912	3,2	7,2	90,1	1,5	0,8615	1,4890	0,8718	1,4914
23	0	135,7	0,8719	1,4919	3,2	10,2	86,8	1,4	0,8645	1,4906	0,8719	1,4920
14	10	143,0	0,8730	1,4920	4,0	13,3	82,9	2,0	0,8666	1,4920	0,8746	1,4921
24	20	139,5	0,8739	1,4924	4,6	11,6	84,3	2,1	0,8658	1,4915	0,8744	1,4926
27	30	141,0	0,8762	1,4927	4,3	16,1	80,1	2,4	0,8658	1,4926	0,8748	1,4928
28	40	126,0	0,8837	1,4918	6,8	20,9	75,8	1,7	0,8658	1,4918	0,8846	1,4913

ratio of olefins to toluene 1 : 7, and volume ratio of acid to hydrocarbons 0.12, the yield of alkyl product (fraction above 175°) varied from 9.1 to 125.5 wt. % of the olefins taken, with a maximum of 143 wt. % at an acid strength of 96%.

The bromine number of the alkyl product decreased in this case from 30.6 to 2.9. As can be seen from Table 1, raising the temperature from −10 to +40° changes the yield of alkyl product from 131.5 to 126 wt. % based on the olefins taken, with a maximum of 143% at a temperature of 10–15°. At the same time, the bromine number increases with increasing temperature.

Changing the reaction time from 0.5 min. (acid feed time without additional stirring) to 90 min. (feed time plus additional stirring time) at a temperature of 10°, acid concentration 96%, molar ratio of olefins to toluene 1 : 7, and ratio of acid to hydrocarbons 0.12 showed that formation of the alkyl product is practically complete after 30 min.; increasing the reaction time above 60 min. leads to an insignificant decrease in the yield of alkyl product.

When the molar ratio of olefins to toluene is increased from 1 : 0.5 to 1 : 10, the yield of alkyl product rises from 90.2 to 145.8 wt. % based on the initial olefins—at first sharply, reaching 139.9 wt. % already at a molar ratio of 1 : 4,

Fig. 1

Figure 1: Fig. 1

and then only slightly. The bromine number of the alkyl product decreases in this case from 12.4 to 2.9.

A study of the effect of the volume ratio of acid to hydrocarbons from 0.05 to 0.5 at 10°, reaction time 60 min., acid concentration 96%, and molar ratio of olefins to toluene 1 : 7 showed that the yield of alkyl product increases only as the ratio is raised to 0.12, and thereafter remains practically unchanged.

The experiments carried out made it possible to outline the following optimum conditions ensuring the maximum yield of alkyl product: concentration of the initial acid 95-97 wt. % as monohydrate, temperature 10-15°,

reaction time 30-40 min, molar ratio of olefins to toluene 1 : 4-1 : 6, volume ratio of acid to hydrocarbons 0.12.

Under these conditions the yield of alkyl product is 140-143 wt. % based on the initial olefins.

It was previously believed ([5–8]) that, in the alkylation of benzene and toluene with diisobutylene on sulfuric, hydrofluoric, and alkanesulfonic acids, significant depolymerization of the initial olefins takes place—dimers with subsequent alkylation of the aromatic hydrocarbon by the monomer. Experiments carried out on the alkylation of toluene with amylene dimers in the presence of sulfuric acid showed that depolymerization is observed to a much lesser degree than had been assumed. The content in the alkyl product of the 175-220° fraction, which concentrates amyltoluenes, under optimum conditions is not more than 12-13 wt. %.

Fig. 1

In addition, the experiments showed that only the concentration of the initial acid and the reaction temperature have a noticeable effect on the yield of the amyltoluene fraction. With a decrease in the concentration of the initial acid and an increase in the reaction temperature, the yield of the 175-220° amyltoluene fraction increases. Thus, when the concentration is decreased from 100 to 89.5%, the content of the 175-220° fraction in the alkyl product increases from 10.4 to 16.5 wt. %; when the reaction temperature is varied within the range from −10 to +40°, as can be seen from Table 1, it increases from 7.2 to 20.9 wt. % based on alkyl product.

Under conditions close to optimum—temperature 10°, reaction time 60 min, molar ratio of olefins to toluene 1 : 7, and volume ratio of acid to hydrocarbons 0.12 —alkyl products with the following properties were obtained. Undistilled alkyl product: ρ_4^{20} 0.8730; n_D^{20} 1.4920; M 216; bromine number 4.0; maximum aniline point 15°. The 175-220° fraction of the alkyl product: ρ_4^{20} 0.8666; n_D^{20} 1.4920;

M 159.5. The 220–300° fraction of the alkyl product: ρ_4^{20} 0.8746; n_D^{20} 1.4921; M 211. Residue above 300° of the alkyl product: ρ_4^{20} 0.9010; n_D^{20} 1.4930. Figure 1 gives the distillation curve of the alkyl product (n) and the characteristics of its narrow fractions.

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Note: Figure translations are in progress. See original paper for figures.