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Abstract

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OBTAINING XYLENES BY DEALKYLATION AND COUPLED ALKYLATION OF AROMATIC HYDROCARBONS IN THE PRESENCE OF SYNTHETIC ALUMINOSILICATES

In a previous work ([1]), we reported the results of our experimental investigations on the synthesis of xylenes by dealkylation of polymethylbenzenes and alkylation of toluene over aluminosilicates. Solvent from coke-gas production is distinguished by a high content of polyalkyl-aromatic compounds, and the development of a rational method for converting them into valuable low-molecular aromatic hydrocarbons is of practical interest.

In the present communication we give the principal data on the process of catalytic treatment of a mixture of solvent with toluene over synthetic aluminosilicates. The solvent, which is essentially a mixture of polyalkylbenzenes, also contained a certain amount of xylenes and impurities of toluene. From it a fraction boiling above 150° was isolated, which was then used in the experimental work. The polyalkylaromatic fraction of the solvent obtained in this way boiled within the range 149-195°. The characteristics of the solvent were as follows: d_4^{20} 0.8818; n_D^{20} 1.5009; iodine number 20.3; M 123; sulfonatability 100%.

Fractional composition, %	
Initial b.p., 149°	
149-160°	2.84
160-165°	20.15
165-175°	52.51
175-185°	9.25
185-195°	5.75
Residue	7.20
Losses	2.8

The main amount of the product obtained (about 73%) is the 160-175° fraction, which consists chiefly of a mixture of pseudocumene and mesitylene. The somewhat elevated iodine number is due to the presence in the product of a small amount of styrene and indene derivatives. Standard toluene was used as the second component; boiling range 109–111°, d_4^{20} 0.8675, n_D^{20} 1.4966, sulfonatability 100%, bromine number 0.2. The principal part of the experiments was carried out in a laboratory flow-reactor unit under pressure. The scheme and description of this unit had been published earlier (^{1}).

At atmospheric pressure, separate experiments were carried out in a Pyrex-glass reactor with a fluidized bed of microspherical and powdered aluminosilicate catalyst. Such a system proved very convenient for conducting experimental work and made it possible to observe the course of the process directly through the glass and to measure the main process parameters with high accuracy. Electrical heating of the reactor was effected by means of nichrome wire wound around it. The attainment of the prescribed temperature regime required 10–15 min. Throughout the entire height of the fluidized bed in the reactor, temperature constancy was established within fluctuations of not more than $±$1.0°. The recommended system of the laboratory reactor (Fig. 1) is highly convenient and can be used successfully for investigations over wide temperature intervals.

Experiments were carried out with a mixture of solvent and toluene in a weight ratio of 1:2. The influence of pressure, feed rate, temperature, and duration of the reaction cycle was studied, and the optimal

parameters of the xylene regime of the process. At temperatures below 350° only slight formation of xylenes was observed. Toluene did not take any noticeable part in the reaction, and in the course of the process only a small decrease in its amount occurred.

Table 1

Characteristics of the products of catalytic processing of a mixture of coke-oven solvent with toluene

Product characteristic	Feedstock (wt. ratio solvent to toluene 1 : 2), fraction yield, wt. %	Feedstock (wt. ratio solvent to toluene 1 : 2), n_D^{20}	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), fraction yield, wt. %	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), n_D^{20}	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), fraction yield, wt. %	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), n_D^{20}
Initial b.p., °C	104.0	–	66.0	–	45.0	–
<50	–	–	–	–	0.85	1.4868

Product characteristic	Feedstock (wt. ratio solvent to toluene 1 : 2), fraction yield, wt. %	Feedstock (wt. ratio solvent to toluene 1 : 2), n_D^{20}	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), fraction yield, wt. %	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), n_D^{20}	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), fraction yield, wt. %	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), n_D^{20}
50—76	–	–	0.20	1.4509	0.37	1.4849
76—78	–	–	0.10	–	0.94	1.4982
78—83	–	–	1.50	1.4957	6.94	1.4982
83—88	–	–	0.28	1.5001	0.23	1.4981
88—103	–	–	0.71	1.4963	0.80	1.4966
103—108	0.45	1.4962	0.35	1.4969	0.47	1.4961
108—113	64.88	1.4970	63.08	1.4972	48.74	1.4964
113—118	0.13	1.4928	0.22	1.4947	0.27	1.4965
118—125	0.20	1.4912	0.22	1.4948	0.40	1.4934
125—136	0.23	1.4898	0.72	1.4956	1.19	1.4958
136—144	0.22	1.4882	9.37	1.4965	26.92	1.4981
144—149	0.20	1.4868	0.56	1.4971	0.64	1.5011
149—160	1.59	1.4873	1.10	1.4921	1.35	1.4969
160—165	5.03	1.4921	1.99	1.4919	3.35	1.4959
165—175	20.29	1.4988	12.49	1.4979	4.05	1.4992
175—185	2.32	1.5008	1.49	1.4959	0.89	1.4998
185—200	1.99	1.4970	–	–	0.37	1.5019

Product characteristic	Feedstock (wt. ratio solvent to toluene 1 : 2), fraction yield, wt. %	Feedstock (wt. ratio solvent to toluene 1 : 2), n_D^{20}	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), fraction yield, wt. %	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), n_D^{20}	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), fraction yield, wt. %	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), n_D^{20}
Final b.p., °C	194.5	194.5	185.0	185.0	190.0	190.0
Total yield, wt. %	97.53	97.53	94.38	94.38	97.83	97.83
Residue, wt. %	1.90	1.90	4.20	4.20	2.01	2.01
Losses, wt. %	0.57	0.57	1.42	1.42	0.16	0.16
d_4^{20}	0.8689	0.8689	0.8670	0.8670	0.8675	0.8675
n_D^{20}	1.4981	1.4981	1.4988	1.4988	1.4991	1.4991
Iodine number	7.7	7.7	3.6	3.6	2.5	2.5
Sulfurability, %	100	100	100	100	100	100
Group chemical composition, wt. %: Unsaturated	3.8	3.8	1.8	1.8	1.5	1.5

Product characteristic	Feedstock (wt. ratio solvent to toluene 1 : 2), fraction yield, wt. %	Feedstock (wt. ratio solvent to toluene 1 : 2), n_D^{20}	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), fraction yield, wt. %	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), n_D^{20}	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), fraction yield, wt. %	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), n_D^{20}
Group chemical composition, wt. %: Aromatic	96.2	96.2	98.2	98.2	98.5	98.5
Group chemical composition, wt. %: Naphthenes + paraffins	–	–	–	–	–	–
Material balance, wt. %: Catalyst	–	–	94.5	94.5	87.8	87.8
Material balance, wt. %: Coke	–	–	1.8	1.8	4.8	4.8

Product characteristic	Feedstock (wt. ratio solvent to toluene 1 : 2), fraction yield, wt. %	Feedstock (wt. ratio solvent to toluene 1 : 2), n_D^{20}	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), fraction yield, wt. %	Catalyst: pressure 1 atm., temp. 480°, space velocity 0.5 : 1 (experiment 74), n_D^{20}	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), fraction yield, wt. %	Catalyst: pressure 15 atm., temp. 480°, space velocity 0.5 : 1 (experiment 63), n_D^{20}
Material balance, wt. %: Gas	–	–	1.2	1.2	4.2	4.2
Material balance, wt. %: Losses	–	–	2.5	2.5	3.2	3.2

Table 2

Characteristics of the principal aromatic fractions

Product characteristic	Initial mixture	Catalyst, experiment 74	Catalyst, experiment 63	Product characteristic	Initial mixture	Catalyst, experiment 74	Catalyst, experiment 63
Fraction 78–83°				n_D^{20}	1.4970	1.4972	1.4964
Yield, wt. %	–	1.50	6.94	Sulfurability, %	100	100	100
d_4^{20}	–	0.8736	0.8739	Bromine number	0.08	0.08	0.08
n_D^{20}	–	1.4957	1.4982	**Fraction 136–144°**			

Product characteristic	Initial mixture	Catalyst, experiment 74	Catalyst, experiment 63	Product characteristic	Initial mixture	Catalyst, experiment 74	Catalyst, experiment 63
Sulfurability, %	—	—	100	Yield, wt. %	0.22	9.37	26.92
Bromine number	—	—	0.32	d_4^{20}	—	0.8664	0.8653
Fraction 108—113°				n_D^{20}	1.4882	1.4975	1.4981
Yield, wt. %	64.88	63.08	48.74	Sulfurability, %	—	100	100
d_4^{20}	0.8653	0.8666	0.8668	Bromine number	—	0.16	0.08

At temperatures of 450-480°, a more substantial dealkylation of the initial polyalkylbenzenes was observed. Tables 1 and 2 present analytical data for two characteristic catalyzates and their principal aromatic fractions. The application of pressure was of decisive importance. Thus, at atmospheric pressure and a temperature of 480°, as a result of dialkylation of the solvent hydrocarbons, 1.5% benzene and 9.3% xylenes were obtained; increasing the pressure directed the course of the reactions toward the maximum formation of xylenes. At 15 atm and 480°, the catalyzate obtained is characterized by a content of 28% xylenes and about 7% benzene. The yield of catalyzate, gas, and coke, based on the feedstock, was respectively 88, 4.8, and 4.2 wt. %. The gaseous reaction products consisted of a mixture of methane and its homologues with hydrogen. A deep conversion of the solvent hydrocarbons was observed. Part of the toluene was alkylated with formation of xylenes, as a result of which its amount decreased from 64% in the feedstock to 48% in the catalyzate. As can be seen from Table 2, the aromatic fractions obtained under optimal conditions contain practically no unsaturated, paraffinic, or naphthenic hydrocarbons; their bromine number usually ranged from 0.08 to 0.3, and sulfonatability was 100%. Spectral analysis of the xylene fraction of the catalyzate showed that it contained about 25% *p*-xylene, 45-50% *m*-xylene, about 20-25% *o*-xylene, and an insignificant amount of ethylbenzene (not more than 2-3%).

Fig. 1. Laboratory setup of a flow reactor with a boiling bed of microspherical and powdered catalysts. *1*—feed burette, *2*—evaporator, *3*—reactor, *4*—glass filter, *5*—condenser-cooler, *6*—receiver, *7*—flowmeter, *8*—burette for gas collection, *9*—gasometer, *10*, *11*—galvanometers.

Figure 1. Laboratory setup of a flow reactor with a boiling bed of microspherical and powdered catalysts. 1—feed burette, 2—evaporator, 3—reactor, 4—glass filter, 5—condenser-cooler, 6—receiver, 7—flowmeter, 8—burette for gas collection, 9—gasometer, 10, 11—galvanometers

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The process of catalytic treatment of a mixture of solvent with toluene is characterized by the simultaneous occurrence of reactions of dealkylation and coupled alkylation of the initial aromatic hydrocarbons. In addition to the indicated reactions, the dismutation reaction of toluene evidently also takes some part in the formation of xylenes. Part of the polyalkylbenzenes was dealkylated over aluminosilicate with formation of low-molecular aromatic hydrocarbons and gas.

The synthesis of xylenes by dealkylation of polyalkylaromatic hydrocarbons and coupled alkylation of toluene in the presence of synthetic aluminosilicates is a promising process, and its practical application will make it possible to considerably increase the resources of paraxylene and other valuable low-molecular aromatic hydrocarbons.

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