

Some Peculiarities of Alkylation Reactions of Phenol With C₄-Fraction Dimerization Products of Pyrolysis Process

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ARTICLE INFO

Article history:

Received: 5 July 2017;

Received in revised form:

30 July 2017;

Accepted: 8 August 2017;

Keywords

alkylation,
dimerization products,
catalyst,
pyrolysis,
p-alkylphenol

ABSTRACT

Alkylation reactions of phenol with dimerization products of devinylated C₄-fraction obtained by the pyrolysis of low-octane gasoil were studied in the presence of KU-23 catalyst. Alkylation reaction was carried out on the continuous unit. As a result of alkylation reaction, it was studied the influence of temperature, time, initial components mol ratios and catalyst amount on the yield and selectivity. In this case the yield of the target product on phenol was 80.4%, and selectivity on the target product was 95.7%.

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Introduction

The chemical compounds obtained on the basis of alkylphenols have special places among the chemical additives as antioxidants, additives, stabilizers added to polymer materials, oils and fuels. They aren't able to change the colour of polyolefins, have high heat resistance and soluble in oils and fuels [1-3].

At present most of the alkylphenols, used in industry are obtained by alkylation of phenol with polymer distillate. Recently, as polymer distillate application fields have been changed (polymer distillate is used as a gasoil component after destruction), there's a famine of alkylating agent in the field of alkylation reactions [4-6].

The paper deals on the study of alkylation reactions of phenol dimerization products of devinylated C₄-fraction, obtained by pyrolysis of low-octane gasoils in the presence of KU-23 catalyst, with 105-190°C fraction (IDF).

Experimental Part

Phenol and IDF were used as initial raw products for the experiments.

Phenol had been distilled before using.

Phenol and its devinylated C₄-fraction (BIF) obtained by pyrolysis of low-octane gasoil were used as alkylating agent. 40.5% isobutylene oligomers are obtained by dimerization of BIF on zeolite catalyst. 100-190°C fractions of isobutylene oligomers were used for alkylation reaction for the purpose of increasing concentrations of isobutylene dimer trimer in the initial raw product.

BIF dimerization products and IDF hydrocarbon compositions are presented in Tab. 1.

As seen from Tab.1., hydrocarbon composition of BIF dimerization products 100-190°C fraction amounts to 51.32% diisobutylene; that's to say the base product of alkylation of phenol with IDF is para-trioctylphenol.

Physico-chemical properties of IDF: T_{boil.} = 105-190°C; n_D²⁰ 1.4473; ρ₄²⁰ 0.8167 mol. K.120.

Cationit KU-23 (GOST 20298-74) was used as a catalyst for alkylation reaction.

Table 1. BIF dimerization products and IDF hydrocarbon composition.

Hydrocarbons	BIF dimerization products, %	100-190°C frac.
C ₅ -C ₇	1.07	0.68
Iso-octane	0.15	0.54
Diisobutylene	38.78	51.35
Diisobutylene isomer	21.09	27.60
Trimers	32.76	19.83
Tetramers and above	6.17	-

KU-23 (modification of 10/60) contains 55-70% water, it's thermal stability to 170°C. KU-23 is heated to 110°C before application for being water-free. The catalyst activity decreases as a result of separation of sulfogroup from the catalyst under influence of temperature during working process and collecting of resinous substances on it.

Phenol alkylation reactions with IDF were realized in three-necked flask. The alkylate obtained was transferred to Claisen's flask for rectification.

As a result of rectification, firstly, unreacted IDF and phenol (to 200°C) and then the target product under low pressure (5 mm Hg) and other alkylation products are separated. Physico-chemical properties, chemical structures and compositions of the products obtained are determined.

Chromatographic analyses of the reaction and rectification products were carried out on LKhM-72 chromatograph. The column length was 2 m. N-AW-DMC chromaton of the size of 0.2±0.25 mm, purified by acid and silanated by dimethylchlorsilan was taken as a solid carrier, but SE-30 methylsiloxane elastomer of 5% -as a stable phase. Column initial temperature was 50°C, end temperature - 280°C, rate of programming 10°C/min., rate of helium - 50 ml/min, evaporator temperature - 250°C, detector temperature - 300°C, rate of diaphragme film - 60 mm/h.

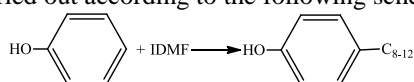
In both of the cases it's important taking of total all peaks fields as 100% for calculating of the amount of initial and end products compositions in percent.

Density of the products synthesized was determined by picnometric, refractive index – on "IRF-22" (Russian Federation) by refractometric methods.

Spectra of the reaction products were taken on Se/Zn crystal, in the range of 600-4000 cm^{-1} wavenumber on ALPHA IR-Fourier spectrometer of "Bruker" company of Germany. NMR spectra were taken on benzene solution deuterated at ambient temperature, at working frequency of 300.18 MHz on Fourier spectrometer of "Bruker" company (Germany). Chemical shifts of the signals were taken according to tetramethylsilane. Relative compositions of different structural fragments protons were determined by integrating of the peaks in corresponding bonds of spectra.

Results and Discussions

Phenol alkylation with IDF in the presence of KU-23 catalyst is carried out according to the following scheme:



The influence of the reaction temperature, time, mol ratios of initial components and catalyst amount on the yield and selectivity of the target product were determined for the purpose of finding out efficient conditions for obtaining para-alkylphenol.

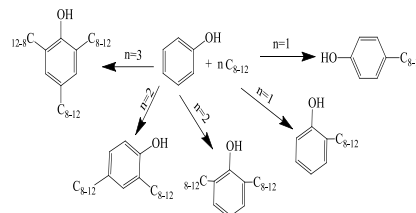
Alkylation reaction temperature was from 60 to 140°C, reaction duration – 2-6 h, phenol and IDF mol ratio – from 2:1 to 2:1, catalyst amount – 5-20%.

The results of phenol alkylation reaction with IDF in the presence of KU-23 catalyst are set into Tab. 2.

As seen from Tab. 2, the by increasing reaction temperature from 60 to 120°C, the yield is changed in the range of 39.3-80.4% (according to the phenol taken), but the reaction selectivity – 87.8-95.7% according to the target product. By increasing of temperature to 140°C, the yield of the target product amounts to 73.9% correspondingly, but selectivity – 87.0%

It's evident from the data of the table, that taking of phenol mol ratio to IDF as 1:2 in the mixture of the components is more reasonable. So, in this case, the yield of the target product is 80.4%, but selectivity – 95.7%. Increasing and decreasing of phenol or IDF concentration in the mixture

of initial components doesn't result effectively in the yield of the target product and selectivity of the reaction. The yield of the target product increases for 2-2.5% by increasing of IDF concentration for 3-4 times. But it's not profitable both from technological and economical points of view. In this case, significant decrease in selectivity is observed; and this is explained according to obtaining 2-mono, 2,4-, 2,6-di and 2,4,6,-tri-substituted alkylphenols as a result of alkylation reaction:



It's also important the influence of meeting time of the initial components mixture on the target product yield and reaction selectivity. As seen from Tab.2, in 5 h duration of the reaction, the yield of the target product amounts to 80.4%, but selectivity – 95.7%.

As seen from the table, optimum yield and selectivity of the target product is achieved in 10% amount of the catalyst. But the yield amounts to 81.7-83.0% and selectivity correspondingly 95.2-88.3% in 15-20% of the catalyst. In the case of increasing of the yield minimally, selectivity decreases at the moment.

So, optimum conditions were found out for phenol alkylation reaction with IDF in the presence of KU-23 catalyst: temperature – 120°C, reaction duration – 5 h, mol ratio of phenol to IDF – 1:2, catalyst amount – 10%. In these conditions, the yield of para-alkyl(C₈₋₁₂)-phenol on the phenol taken amounts to 80.4%, but selectivity on the target product – 95.7%.

Chemical structure of synthesized p-alkylphenol was determined by ¹H-NMR- and IR-spectroscopical methods.

On ¹H-NMR-spectrum of p-alkylphenol singlet CH₃ group was observed at 1.20 ppm, singlet of hydrocarbon ring – at 1.77 ppm, OH-group and multiplet 1,4-substituted benzene ring – at 5-6 ppm bands.

On IR-spectrum of p-alkylphenol the following bands were observed: 1505, 1592-1610 cm^{-1} (benzene ring), 3010, 3030 cm^{-1} CH₂ = valence vibrations, 825 cm^{-1} (CH₂-deformational vibrations).

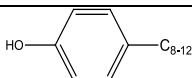
Table 2. Results of phenol alkylation reactions with IDF in the presence of KU-23 catalyst on the continuous unit.

Exp. №-	Taken, g		Reaction condition			Obtained, g				Yield of MM, %	Selectivity, %
	Phenol	IDF	Temp., °C	Time, h ⁻¹	Catalyst amount, %	Returned IDF	Returned phenol	TP	SP		
1.	47	120	60	4.5	10	23.4	94.6	42.1	3.2	39.3	87.8
2.	47	120	80	4.5	10	20.3	77.8	61.6	3.2	57.6	91.2
3.	47	120	100	4.5	10	18.5	62.8	78.3	3.1	73.2	93.5
4.	47	120	120	4.5	10	15.7	59.6	86.0	2.0	80.4	95.7
5.	47	120	140	4.5	10	15.1	58.2	79.1	6.3	73.9	87.0
6.	47	120	120	2	10	22.7	94.5	46.9	0.9	43.8	96.7
7.	47	120	120	3	10	19.8	76.4	65.9	1.5	61.6	96.1
8.	47	120	120	4.5	10	15.7	59.6	86.0	2.0	80.4	95.7
9.	47	120	120	6	10	13.1	55.0	82.5	6.3	77.1	86.3
10.	47	60	120	4.5	10	12.0	17.8	67.1	3.0	62.7	88.6
11.	47	120	120	4.5	10	15.7	59.6	86.0	2.0	80.4	95.7
12.	47	180	120	4.5	10	8.7	132.2	78.1	2.7	73.0	94.3
13.	47	240	120	4.5	10	14.3	188.5	65.6	5.8	61.3	80.7
14.	47	120	100	4.5	5	17.7	72.7	72.7	1.2	67.9	97.3
15.	47	120	100	4.5	10	15.7	59.6	86.0	2.0	80.4	95.7
16.	47	120	100	4.5	5	13.7	58.7	87.4	2.2	81.7	95.2
17.	47	120	100	4.5	20	11.3	51.6	88.8	4.7	83.0	88.3

OH-group is observed at 1240 cm^{-1} and $3100\text{-}3500\text{ cm}^{-1}$ bands. Substituted tricarbon is observed both in C-H valence vibrations $2920\text{-}2845\text{ cm}^{-1}$ bands and simultaneously δ_{CH_2} characterizing 1108, 1345 bands. Methyl groups are characterized by deformational vibrations at $1370\text{-}1460\text{ cm}^{-1}$.

Physico-chemical properties of para-alkyl(C_{8-12})-phenol is presented at Tab. 3.

Table 3. Physico-chemical properties of para-alkyl(C_{8-12})-phenol.

Structural formula	T _{boil.} C/ 5 mm Hg	n _D ²⁰	ρ ₄ ⁴⁰	Mol. weight
	140-160	1.5445	1.0040	280

Conclusion

Phenol alkylation reactions with IDF were studied in the presence of KU-23 catalyst. There were determined that the yield of para-alkyl (C_{8-12})-phenol on the phenol taken amounts to 80.4%. but the reaction selectivity on the target product - 95.7% at optimum conditions of the reactions – temperature of 120°C , the reaction duration – 5 h, 1:2 mol ratio of phenol to IDF and 10% of the catalyst.

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