SUSPENSION OLIGOMERIZATION OF THE HYDROCARBON FRACTION C9 INITIATED BY 2-[4-(TERT-BUTYLPEROXYMETHYL) PIPERAZINOMETHYLPEROXY]-2-METHYLPROPANE

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The production of hydrocarbon resins by low-temperature oligomerization in an suspension initiated by 2-[4-(tert-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane is considered. Correlation dependences between yield, resin characteristics and process conditions are established.

Keywords – petroleum resin, suspension oligomerization, fraction C9, bromine number, oil processing.

Introduction

In the process of synthesis of ethylene/propylene by pyrolysis, a significant number of liquid by-products (about 30%) are obtained. C9 fraction, containing unsaturated aromatics (styrenes and indenes), to produce aromatic oligomers. Aromatic oligomers (so-called petroleum or hydrocarbon resins) have a wide range of applications as film-forming agents in lacquer-paint and anticorrosive coatings [1, 2].

We propose to use the suspension method of oligomerization of unsaturated hydrocarbon of C9 fraction of diesel pyrolysis liquid by-products. This method can significantly reduce the process temperature and reaction time compared to the industrial methods of oligomers (hydrocarbon resins) synthesis [1]. This method is characterized by a low temperature of the process (303–353 K) and makes it possible to get oligomers with a low color index.

Experimental results and discussion

Composition of the reaction mixture of suspension oligomerization: the dispersion medium - water; the disperse phase – fraction C9; the initiator is soluble in the disperse phase; suspension stabilizer - polyvinyl alcohol (0.1 %wt)

Fraction C9 properties: density – 936 kg/m^3; bromine number – 68 g Br_2/100 g, molecular weight – 102, the content of unsaturated compounds to 45 %wt. especially: styrene - 17,85 % viniltoluene - 6,99 %, dicyclopentadiene - 18,00 %, indene 1,25 %.

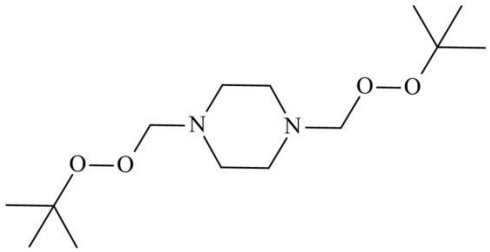

Fig. 1. Aminoperoxide initiators with cyclic substituents – 2-[4-(tert-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane

Initiator properties: active oxygen – 9.65 %, refractive index – 1.4590. Thermolysis occurs in 2 stages. Stage 1: 305–355 K, weight loss – 19.02 %, kef=1.4·10–2; stage 2: 356–386 K, weight loss – 51.04 %, kef=5.0·10-2.

Suspension oligomerization was carried out at pre-established optimal values of mixing intensity (Re = 10120) and volume ratio dispersion phase – dispersion medium (1:2). The

dependence of the oligomers' yield and properties of synthesized oligomers on on reaction conditions is given in Table 1

Table 1

Experimental data on the suspension oligomerization of the C9 fraction initiated by 2-[4-(tert-butylperoxymethyl) piperazinomethylperoxy]-2-methylpropane

Reaction temperature, K	Reaction duration, min	Concentration of the initiator, mol/l	Yield, %wt.	Bromine number $gBr_2/100$ g	Softening temperature, K	Molecular weight
318	180	0.032	13.6	36.3	354	515
		0.064	16.6	33.4	348	510
		0.096	15.2	32.3	348	510
333	180	0.032	19.1	32.2	352	515
		0.064	20.1	35.1	347	505
		0.096	19.9	34.8	350	510
353	30	0.032	5.0	45.6	360	530
	60	0.032	8.3	41.3	360	525
	120	0.032	14.2	36.0	358	520
	180	0.032	19.4	35.6	353	520
	240	0.032	19.8	35.7	359	525
Correlation with reaction temperature			–0,23	0.29	0.62	0.40
Correlation with the initiator concentration			0.50	–0.36	–0.67	–0.73
Correlation with reaction time			0.74	–0.87	–0.54	–0.46

The color indicator of suspension oligomerization products in the studied intervals varies slightly and is 20–30 mg I_2/100 ml (7–8 on the Gardner scale).The decrease in the bromine number of hydrocarbon resins correlates with an increase in yield (–0.83).

According to the chromatographic analysis of the initial C9 fraction and the obtained distillates suspension oligomerization products are co-oligomers of styrene and its derivatives.

Conclusion

It is established that under the investigated oligomerization conditions in the suspension, an increase in the temperature of the reaction to 353 K does not affect the yield of the oligomer, which allows the process to be carried out at a temperature of 303 K. The optimal conditions for suspension oligomerization: reaction temperature, 333 K; reaction duration, 180 min; initiation concentration, 0.032 mol/l. Under such conditions, oligomers are obtained with a color of 20 mg I_2/100 ml at the oligomer yield of 19.1 %.

References

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