Synthesis of Styrene and Cyclopentadiene (Co)oligomers on the Basis of Fraction C9 of Oil Refining By-products

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Abstract – The production of styrenic and cyclopentadiene co-oligomers by oil refining by-products (hydrocarbon fraction C9) oligomerization studied. The combination of methods of low temperature suspension oligomerization and post-(co)oligomerization of unreacted hydrocarbons allow to obtain, on the basis of the hydrocarbon fraction C9, the styrenic and cyclopentadiene (co)oligomers, which differ in their properties and applications.

Keywords – liquid pyrolysis products, suspension (co)oligomerization, hydrocarbon fraction C9, cyclopentadiene, styrene.

Introduction

A significant amount (about 30%) of liquid by-products of pyrolysis (LBP) is formed at petroleum products pyrolysis (e.g. diesel fuel). Based on LBP hydrocarbon fraction C9 respectively, are obtained aromatic oligomers (so-called petroleum resins). They have a wide range of applications as film forming agents in lacquer-paint and anticorrosive coatings [1, 2].

The low-temperature suspension oligomerization can reduce the temperature and duration of the process compared to the existing technologies. Due to the low temperature of the process, the styrene monomers and their derivatives are introduced into the reaction. The resulting hydrocarbon resin is a styrenic (co)oligomer and is characterized by a low color index. Dicyclopentadiene (DCPD) is inactive in radical polymerization reactions. Cyclopentadiene (CPD) is polymerized by free radical mechanism. A cycle is revealed (monomerization) of the DCPD at temperatures 453-463 K with the formation of two reactive CPD monomers, by retro-dyenic reaction Diels-Alder synthesis [3, 4].

We proposed a two-stage method (Fig.1) for the synthesis of (co)oligomers of styrene and cyclopentadiene [5]:

Fig.1. Two-stage method for the synthesis of co-oligomers of styrene and cyclopentadiene

- the first stage – low-temperature (303-353 K) suspension or emulsion cooligomerization of fraction C9 hydrocarbons. At this stage, a styrenic (co)oligomer is obtained.
- the second stage is the thermal or initiated post-cooligomerization of unreacted hydrocarbons from the first stage. The temperature of the process is 453-473 K. At this stage, a cyclopentadiene (co)oligomer with a small number of parts of other unsaturated hydrocarbons of the C9 fraction is obtained.

Experimental Results and Discussion

Composition of the reaction mixture of suspension oligomerization:

- the dispersion medium - water;
- the disperse phase – liquid pirolisis by-products fraction C9 (density – 936 kg/m³; bromine number – 68 g Br₂/100 g, molecular weight – 102, the content of unsaturated compounds to 45 %wt. especially: styrene - 17,85 % vinyltoluene - 6,99 %, dicyclopentadiene - 18,00 %, indene 1,25 %.);
- the initiator is soluble in the disperse phase (1,0 %wt. calculated on the C9 fraction);
- suspension stabilizer – polyvinyl alcohol (0,1 %wt. calculated on the dispersion medium).

The suspension oligomerization of the C9 fraction was carried out in a three-necked flask equipped with a rotary stirrer. The resulting mixture was separated by centrifuge (4000 rpm).

Post-(co)oligomerization was carried out in thermostatically controlled sleeves at a temperature of 453 K for 6 hours, with the addition of a suitable initiator in an amount of 1.0% by weight. The choice of temperature is due to the composition of the fraction, namely the presence of a significant amount of dicyclopentadiene (about 13.6% by weight, calculated on the initial fraction) and its homologues. Unreacted hydrocarbons were isolated by atmospheric and vacuum distillation.

For the obtained (co)oligomers yield (calculated on the C₉ fraction), unsaturation (bromine number), color index by iodometric scale, softening temperature and average molecular weight were determined. The results are shown in Table. 1.

Suspension (co)oligomerization of unsaturated hydrocarbons of C9 fraction (first stage) ensures maximum yield of the product - up to 19.0% by weight (calculated on the C₉ fraction). Chromatographic analysis revealed that at first stage, the styrene monomers and its derivatives (vinyltoluene, methylstyrene) are introduced into the cooligomerization reaction. In the reaction mixture remaining after the separation of the (co)oligomer and distillation of the precipitant there are high-boiling reactive dicyclopentadiene, indene, residual styrene and its derivatives.

As a result of initiated high-temperature post-(co)oligomerization of unreacted residues (second stage) was obtained hydrocarbon resins with a high content of cyclopentadiene units. The cyclopentadiene (co)oligomer contains insignificant quantities of styrene and vinyl-toluene units that did not react at the first stage of the process.

The cyclopentadiene (co)oligomers obtained at the second stage is characterized by a lower index of unsaturation (22,2 - 27,8 g Br₂ / 100 g), a similar softening temperature (350-358 K), a higher average molecular weight (640 - 700) and a significantly higher color index - 60 ... 80 mg I₂ / 100 ml (compared to styrenic (co)oligomers).

The composition of the (co)oligomers was determined basing on the data of the IR-spectroscopic analysis of the (co)oligomers samples of and the chromatographic analyzes of the C9 fraction and distillates.

Table 1

Yield, physical and chemical properties of (co)oligomers

Characteristics	Initiator		
	Benzoyl Peroxide	<i>tert</i> -Butyl Hydroperoxide	Cumyl Hydroperoxide
Suspension (co)oligomerization ([fraction C9] : [water] = 1:2; T = 353 K; τ = 3 hours; C _{initiator} = 1,0 % wt.; C _{stabilizer} = 0,1 % wt.)			
Styrene (co)oligomer yield, % by weight (calculated on the C9 fraction)	19,0	9,8	16,0
Bromine number, g Br ₂ / 100 g	30,3	32,0	19,9
Softening point, K	354	340	350
Molecular weight (cryoscopy)	495	460	490
Color by iodometric scale, mg I ₂ /100 ml	20	30	30
Post-co-oligomerization (C _{initiator} = 1,0 % wt., T = 453 K, τ = 6 hours)			
Cyclopentadiene (co)oligomer yield, % by weight (calculated on the C9 fraction)	19,8	30,1	25,7
Bromine number, g Br ₂ / 100 g	20,4	22,8	23,4
Softening point, K	358	354	350
Molecular weight (cryoscopy)	700	640	670
Color by iodometric scale, mg I ₂ /100 ml	80	80	80
Total yield, % wt. (calculated on the C9 fraction)	38,8	39,9	41,7

Conclusion

The possibility of synthesis of styrenic and cyclopentadiene co-oligomers by two-stage method of oil refining by-products (hydrocarbon fraction C9) oligomerization was established. The two-stage method of the C9 fraction oligomerization allows to obtain two types of oligomers with different physical and chemical characteristics. The total yield of oligomers is higher than with one-stage initiated high-temperature oligomerization.

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