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ТЕХНОЛОГІЯ ОРГАНІЧНИХ РЕЧОВИН, ТЕХНОЛОГІЯ ПЕРЕРОБКИ НАФТИ ТА ГАЗУ

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C9 FRACTION INVERSE EMULSION OLIGOMERIZATION CONDITIONS AND CHARACTERISTICS OF PETROLEUM RESINS CORRELATION

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It has been studied the production of petroleum resins by low-temperature inverse emulsion oligomerization of C9 fraction of diesel fuel pyrolysis liquid by-products. It is established that the determining factors of the C9 fraction of the inverse emulsion oligomerization are the following: reaction time, emulsifier concentration and phase ratio. Yield and physicochemical characteristics of oligomers correlations were established. Multiple linear regression of oligomer yield depends on the main significant parameters of the fraction C9 inverse emulsion oligomerization is proposed.

Key words: liquid pyrolysis by-products; petroleum resin; inverse emulsion; oligomerization; fraction C9; emulsifier; correlation.

Introduction

In the process of synthesis of ethylene/propylene by diesel fuel pyrolysis, a significant number of liquid by-products (about 30–35 %) are obtained. The following pyrolysis fractions are used as raw materials for oligomers (petroleum resins) production [1, 2]:

- C4 fraction, containing olefins to produce polybutene resins;
- C5 fraction containing linear and cyclic olefins, to produce aliphatic resins (aliphatic petroleum resins);
- C9 (C8/C9) fraction, containing unsaturated aromatics (styrenes and indenes), to produce aromatic oligomers.

Aromatic oligomers (so called petroleum or hydrocarbon resins) [3]. They have a wide range of applications as film-forming agents in lacquer-paint and anticorrosive coatings for bitumens modification [4, 5].

We suggest to use the emulsion 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. This process is preferred because the reaction medium (which is usually water) makes it easier to promote mixing, heat, mass transfer and provides a safe process [6–8].

Emulsions are characterized by the property of phase reversal. In the case of introduction into the emulsion under conditions of intensive mixing of surfactants, emulsifiers of the opposite kind, the original emulsion may be treated. The dispersed phase becomes a dispersion medium and vice versa [9, 10].

According to the polarity of the phases, there are two types of emulsions:

- direct (an emulsion of the first kind), which consist of a polar dispersion medium – water and non-polar dispersed phase – oil (denote “oil-in-water”);
- inverse (second kind emulsion), in which the dispersion medium is non-polar – oil, and the dispersed phase is polar – water (denote “water-in-oil”) [10].

The efficiency of the emulsifier can be characterized by the ratio of the hydrophobic and hydrophilic particles of surfactant molecules (HLB – hydrophilic-lipophilic balance). HLB is an empirically dimensionless quantity [11].

The usage of an emulsion of the second kind (inverse emulsion or “water-in-oil” emulsion) allows reducing the amount of water in the reaction mixture. This increases the productivity of the reaction equipment and reduces energy consumption. A necessary condition for the formation of an emulsion of the second kind [fraction C9 – water] is the presence of oil-soluble emulsifiers, which are used to form an emulsion of the “water-in-oil” kind.

They are characterized by the value of HLB from 3 to 6 [10, 11].

The aim of the study

Study of the basic regularities and determination of the influence of the main factors on the course of low-temperature fraction C9 of liquid by-products of pyrolysis of diesel fuel. Analysis of of oligomerization factors and conditions in the emulsion with the yield and properties of hydrocarbon resins correlation.

Establishing yield of hydrocarbon resin and its characteristics correlations.

Materials and methods of research

Hydrocarbon fraction C9 c of diesel pyrolysis liquid by-products characteristics: bromine number – 67 g Br_2/100 g, density – 935 kg/m^3; molecular weight – 104, the content of styrene and its derivatives – 25.9 %wt. (styrene – 16.5 %wt, viniltoluene – 6.1 %wt, α-methylstyrene – 2.0 %wt, allylbenzene – 1.3 %wt).

Composition of the reaction mixture of 2nd kind emulsion oligomerization:

- the dispersing medium – liquid pyrolysis by-products fraction C9;
- the disperse phase – water;
- emulsifier – used emulsifiers of the second kind that form an emulsion such as “water-in-oil”: Polyglycerol Polyricinoleate – HLB = 6; “Ester A” (a mixture of mono- and di-glycerides of oleic acid) – HLB = 3.
- the initiator is soluble in the dispersing medium (inverse emulsion) – Benzoyl Peroxide 1.0 %wt. (in terms of fraction C9).

The pH of the reaction mixture is 2.8 (without buffer additives). The main studied process parameters:

- the reaction temperature was 303, 318, 323, 333 K;
- the reaction time – 20, 40, 60, 120, 180 min;
- the emulsifier concentration – 0.6–1.0 % (in terms of water);
- stirring (Re = 6870–10120);
- the volume ratio fraction C9: water – [1:1], [2:1], [3:1], [4:1], [5:1].

The composition of the obtained hydrocarbon resins was determined based on the data of the IR-spectroscopic analysis of the petroleum resins samples and the chromatographic analyzes of the C9 fraction and distillates. It is established that the composition of such hydrocarbon resins includes styrene and its derivatives (vinyltoluene, methylstyrene and others).

Due to the low temperature (303–333 K) of the inverse emulsion oligomerization, the styrene monomers and their derivatives are introduced into the reaction. Under conditions of emulsion oligomerization (temperature below 453 K) dicyclopentadiene (DCPD) is inactive in radical polymerization reactions. A DCPD cycle is revealed (monomerization) at temperatures 453–463 K with the formation of two reactive cyclopentadiene monomers by retro-dyenic reaction Diels-Alder synthesis [12].

The mixture of unreacted hydrocarbons will be enriched with dicyclopentadiene. Such a mixture can be used as raw material for cyclopentadiene (co)oligomer synthesis by thermal (453–473 K) or initiated oligomerization [13, 14].

Dispersion oligomerization was carried out in a three-necked flask equipped with a rotary stirrer and a reflux condenser. After loading the components, the reaction mixture was stirred vigorously (Re = 6870–10120) and maintained at a given temperature. After completion of the experiment and stopping mechanical stirring, the reaction mixture was partially separated. The peeled aqueous layer was separated on a separating funnel. Centrifugation (4,000 min^{-1}) was used to separate the final emulsion. The centrifuge separated oligomers were dried in an oven at 323–343 K and the yield of the oligomers was calculated.

If necessary, the oligomerizate (organic phase) separated by atmospheric (pressure – 0.11 MPa, cube temperature – 453 K) and vacuum (residual pressure – 3–4 hPa, cube temperature – 450 K) distillation of the oligomerizate. An oligomer was obtained in a distillation cube.

The obtained oligomers (petroleum resins) were evaluated according to the following indicators: yield (in terms of fraction C9), unsaturation (bromine number), softening point/temperature ("rings and balls" method), average molecular weight (cryoscopy, solvent – benzene), color index(by iodometric scale).

The synthesized petroleum resins (oligomers) meet the requirements of ТУ У 6-05743160.020-99 for resin oil-based synthetic paint.

Results and Discussion

Microsoft Excel 365 was used to calculate statistical indicators of the obtained results of experimental researches and correlation indicators. A number of rows of variables – 67. Calculated: average value, maximum/minimum value, average linear deviation, etc. The results are shown in Table 1.

Table 1 shows a statistical analysis of experimental studies of the C9 fraction inverse emulsion oligomerization. 67 results of experimental researches were selected for the statistical analysis. These experiments differed in different conditions namely: temperature and duration of the reaction, stirring intensity, the volume ratio of the dispersion medium – disperse phase and the concentration of the emulsifier.

Table 1

Statistical analysis of the yield and physicochemical characteristics of hydrocarbon resins

Specifications	Yield, %wt.	Bromine number), $gBr_2/100g$	Color by iodometric scale, mg I_2/100 ml	Softening point, K	Molecular weight
average value	8.81	47.61	23.86	357.44	564.04
maximum value	18.00	62.57	40.00	365.00	600.00
minimum value	1.00	31.30	20.00	340.00	495.00
average linear deviation	4.44	7.48	5.42	3.87	19.22
population variance	27.28	79.29	41.24	23.09	611.79
the sample variance	27.77	80.71	41.98	23.50	622.71
general standard deviation	5.22	8.90	6.42	4.81	24.73
selective standard deviation	5.27	8.98	6.48	4.85	24.95
variation coefficient	0.60	0.19	0.27	0.01	0.04

Table 2

Correlation of petroleum resins characteristics and reaction conditions

Characteristic	Correlation index				
	reaction duration	temperature	emulsifier concentration	phase ratio	mixing intensity
Yield	0.81	0.30	0.03	0.51	0.51
Bromine number	–0.83	–0.27	0.08	–0.57	–0.06
Molecular weight	–0.28	0.02	0.59	0.24	0.05
Softening point	0.11	0.15	0.31	0.23	–0.05
Color index	0.54	0.45	–0.52	0.05	–0.26

As confirmed by the average correlation indices (per module), the emulsion oligomerization temperature has the least effect on the process. The most significant effect (0.81) on the yield of oligomers has the reaction duration. This is consistent with the known theoretical data on the constant rate of emulsion polymerization [10]. Significant correlation index (0.51) with the oligomer yield have the volume ratio of the phases, and the mixing intensity. The reaction temperature and the concentration of emulsifiers in the study range do not significantly affect the yield of oligomers.

Multiple linear regression is suggested. For its construction, the parameters that have the most significant impact on the course of the oligomerization reaction are selected. The calculations were performed by the method of least squares (LINEST function in Microsoft Excel).

Table 3

Factors identified multiple linear regression

b0	–8.9825
The reaction duration (*D*)	0.0603
The volume ratio of the phases (*R*)	0.0924
The mixing intensity (*M*)	0.0046

The calculated Fisher criterion is 95.593. It`s indicates the high adequacy of the proposed multiple linear regression [15, 16].

The dependence of the oligomer yield (*Y*) on the considered parameters (multiple linear regression) is described by the equation:

$$Y = -8.9825+D\times0.0603+R\times0.0924+M\times0.0046.$$

Increasing the duration of the oligomerization (up to 180 min) increases of the oligomer yield. Increasing the proportion of water in the mixture leads to a decrease in product yield. The optimal value of the ratio is [4:1]. The optimal mixing intensity is *Re* = 10120.

The yield and physicochemical properties of petroleum resins are interrelated. For example, an increase in the molecular weight medium and a narrowing of the molecular weight distribution cause an increase in the softening temperature of the oligomers.

Table 4

Correlation of petroleum resins characteristics

Characteristic	Yield	Bromine number	Color index	Softening point	Molecular weight
Yield		–0.94	0.2810	0.3186	0.1041
Bromine number			–0.4253	–0.2737	0.0150
Color				–0.0890	–0.5453
Softening point					0.7320
Molecular weight					

The highest correlation index (0.94 per module) is observed for the yield-bromine number pair. This indicates the course of the oligomerization reaction on unsaturated bonds of monomers. This confirms the actual oligomerization reaction.

The color index and molecular weight (0.81) have no significant correlations with the yield. The color index has low correlation values to other characteristics. The color of petroleum resins in particular depends on the stage of isolation and drying of the product.

There is a high rate of correlation of the average molecular weight and softening temperature (0.73). This is due to the possibility of separation at the stage of drying unpolymerized monomers and low molecular weight dimers, trimmers.

Conclusions

Petroleum resins were obtained by oligomerization in an emulsion of the second kind. Experiments differed in different conditions namely: temperature and duration of the reaction, stirring intensity, the volume ratio of the fraction C9 – water and the emulsifier concentration. The main correlations of the reaction conditions and the yield and characteristics of petroleum resins are established.

It was established that the product yield depends on all process conditions. There is no single decisive parameter of the process. However, it is possible to identify the parameters that have the most significant impact on the course of the reaction. In the case of oligomerization in an emulsion of the second kind, the following are significant: reaction time, emulsifier concentration and phase ratio. The color of petroleum resins in particular depends on the stage of isolation and drying of the product. Multiple linear regression of oligomer yield depends on the main significant parameters of the fraction C9 inverse emulsion oligomerization process is suggested.

The yield and hydrocarbon resins properties correlate with each other.

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КОРЕЛЯЦІЯ УМОВ ЗВОРОТНОЇ ЕМУЛЬСІЙНОЇ ОЛІГОМЕРИЗАЦІЇ ФРАКЦІЇ С9 ТА ХАРАКТЕРИСТИК НАФТОПОЛІМЕРНИХ СМОЛ

Досліджено виробництво нафтополімерних смол за допомогою низькотемпературної зворотної емульсійної коолігомеризації фракції С9 рідких побічних продуктів піролізу дизельного палива. Встановлено, що визначальними факторами частки С9 зворотної емульсійної олігомеризації є тривалість реакції, концентрація емульгатора та фазове співвідношення. Розраховано кореляцію виходу та фізико-хімічних характеристик олігомерів. Запропоновано множинну лінійну регресію виходу олігомеру залежно від основних значущих параметрів процесу олігомеризації у зворотній емульсії.

Ключові слова: рідкі продукти піролізу; нафтополімерна смола; зворотна емульсія; олігомеризація; фракція С9; емульгатор; кореляція.