

ТЕХНОЛОГІЯ ОРГАНІЧНИХ РЕЧОВИН, ТЕХНОЛОГІЯ ПЕРЕРОБЛЕННЯ НАФТИ ТА ГАЗУ

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COMPARATIVE STUDY OF THE HYDROCARBON RESINS PRODUCTION OF BY THE C9 FRACTION EMULSION AND SUSPENSION OLIGOMERIZATION

<https://doi.org/>

The production of a hydrocarbon resins (co-oligomers) by low-temperature dispersion co-oligomerization of C9 fraction of diesel fuel pyrolysis liquid by-products was researched. This method allows to reduce the temperature of the process. The synthesis was carried out by emulsion and suspension co-oligomerization. The main regularities of the suspension and emulsion oligomerization of the hydrocarbon fraction C9 are established. The effect of temperature, initiator concentration and process duration on the yield, physical and chemical properties of synthesized oligomers were investigated. The features of the course of emulsion and suspension oligomerization are compared.

Key words: oligomerization, emulsion, suspension, petroleum resin, hydrocarbon resin, initiator, Potassium Persulfate, Benzoyl Peroxide.

Introduction

The C9 hydrocarbon fraction is obtained by fractionation of the pyrocondensate (lightweight resin) of ethylene production by-products. The production of ethylene by pyrolysis of petroleum raw materials (gasoline and diesel) produces 30–35 % of the liquid by-products of pyrolysis (LBP). The LBP are divided into light pyrolysis resin (~ 80 %) and heavy pyrolysis resin. From the pyrocondensate, in particular, the C9 fraction with an interval of boiling points is isolated – 423–473 K [1, 2].

The C9 fraction is both a mixture of monomers and a solvent (non-resin forming hydrocarbons). Hydrocarbon resins, also known as “petroleum resins”, are obtained by radical initiated, radical thermal (without initiator) and ionic oligomerization methods [3]. As a result of oligomerization, oligomerize is obtained – a solution of hydrocarbon resin in the unpolymerized hydrocarbons fraction [4]. The target product is a hydrocarbon resin, obtained after separation (distillation or precipitation) from solu-

tion, and is a styrene-cyclopentadiene co-oligomer. Such oligomers are used as film-forming agents in lacquer-paint coatings and anti-corrosion compositions, for bitumens modification [5, 6].

The existing industrial methods for preparing such oligomers have a number of disadvantages. The main disadvantage of catalytic oligomerization is the high color ratio and the need to separate the heterogeneous catalyst. The disadvantage of radical co-oligomerization (thermal and initiated) are significant duration of the oligomerization reaction (6–8 hours) and the high temperature of the process (453–473 K). In all cases, the hydrocarbon resin is separated from the oligomerize by distillation from a solution of unpolymerized fraction components [3].

To eliminate the disadvantages of industrial methods, we have proposed the use of low-temperature dispersion oligomerization of the hydrocarbon fraction [7].

Low-temperature (303–333 K) emulsion and suspension oligomerization enables the oligome-

rization hydrocarbons reaction dispersed in water. The hydrocarbon resins thus obtained are characterized by a low color index (10–20 mg I₂/100 ml by iodometric scale) and a narrow range of molecular weight distribution [7, 8].

We proposed a two-stages synthesis method. This method makes full use of the hydrocarbons of fraction C9. The total yield of the products in two stages is higher than for the one-stage industrial process of high-temperature initiated oligomerization.

Stage 1 – include low-temperature (333–353 K) suspension or emulsion fraction C9 hydrocarbons co-oligomerization. At stage 1 a styrenic (co)oligomer is obtained [9].

Chromatographic analysis of the hydrocarbon resins (obtained by low-temperature dispersion oligomerization) and the unreacted fraction of C9. It was established that the styrene and its derivatives are involved into the cooligomerization reaction. In C9 fraction after oligomerization, there are high-boiling components: indene, dicyclopentadiene, residual styrene and its derivatives.

This is due to the fact that dicyclopentadiene (DCPD) does not polymerize by a radical mechanism. In the polymerization and copolymerization reaction, its monomer – cyclopentadiene, enters. A DCPD cycle is revealed by retro-diene reaction Diels-Alder synthesis at temperature about 453 K. As a result, two reactive cyclopentadiene (CPD) monomers are formed. Indene and its derivatives reactive close to DCPD. [10, 11].

For more complete use of hydrocarbons of the fraction we carry out stage 2 – high-temperature (453–473 K) initiation post-cooligomerization of unreacted hydrocarbons. The resulting cyclopentadiene co-oligomer is characterized by a small number of indene parts and residues of other unsaturated hydrocarbons of the C9 fraction [9].

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 emulsion and suspension co-oligomerizations of hydrocarbons of fraction C9 of liquid by-products of pyrolysis of diesel fuel. Comparative evaluation of dispersion methods of fraction C9 oligomerization.

Materials and methods of research

Hydrocarbon fraction C9 characteristics: bromine number – 67 g Br₂/100 g, density – 935 kg/m³; molecular weight – 104, the content of styrene and its derivatives – 25,9 % wt. (styrene – 16,5 %, vinyltoluene – 6,1 %, *p*-methylstyrene – 2,0 %, allylbenzene – 1,3 %).

The reaction temperature was 303–353 K, concentration of initiators 0.5–1.5 % wt. (in terms of fraction C9), the reaction time was 180 minutes. Dispersed phase – C9 hydrocarbon fraction of diesel fuel pyrolysis products; dispersion medium is water. The volume ratio dispersed phase: dispersion medium = [1: 2] (selected based on previous research). The pH of the reaction mixture is 2.8.

Emulsion oligomerization was performed using a water-soluble initiators – Potassium Persulfate (PP) and Hydrogen Peroxide (HP) (0.5–1.5 % wt. in terms of the dispersed phase) and anionic emulsifier of the first kind – E-30 (0.7 % wt. in terms of the dispersion medium). E-30 is a mixture of linear C15 alkanesulfonates of the general formula R-SO₃Na.

To initiate suspension oligomerization used Benzoyl Peroxide (BP) and di-*tert*-Butyl Peroxide (DTBP) (0.5–1.5 % wt. in terms of the dispersed phase) was used. To stabilize the suspension was used polyvinyl alcohol (0.1 % wt. in terms of dispersion medium).

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 = 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.

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

Results and Discussion

As a result of experimental studies of the dispersion of oligomerizations over time, the dependence of the oligomerizate density on the reaction duration was obtained (Fig. 1).

The initial density of the hydrocarbon fraction is 902 kg/m^3 . The oligomerizate density correlates with the oligomer yield. Increasing the oligomerizate density corresponds to an increase in the amount of the high molecular weight compound.

As shown in Fig. 1 in the process of suspension oligomerization, the density of the oligomerizate increases rapidly during the first 60 minutes (from 902 to 916 kg/m^3). Over the next 120 minutes, the growth of oligomerizate density is low (about $4\text{--}2 \text{ kg/m}^3$). Dynamics of change in the density of oligomerizate in suspension oligomerization corresponds to the theoretical provisions [12].

For the emulsion oligomerization, the graph of the dynamics of the change of the oligomerizate density is linear. Which indicates a constant uniform increasing in the density of the oligomerizate. This indicates a stable uniform rate of oligomerization reaction in the test range. This corresponds to known theoretical data on the rate of emulsion polymerization [13].

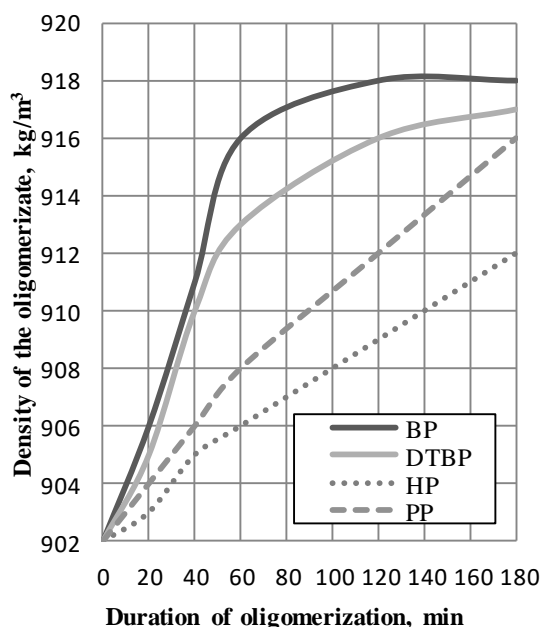


Fig. 1. Dynamics of change in the density of oligomerizate in suspension and emulsion oligomerization ($T = 323 \text{ K}$; [fraction C9] : [water] = 1:2; $Re = 10120$; $C(\text{initiator}) = 1,0 \text{ wt.}$)

The following studies were performed with an oligomerization duration of 180 min.

To establish the effect of the reaction temperature on the course of the emulsion and suspension oligomerization studies were conducted in the temperature range $303\text{--}353 \text{ K}$ for 180 minutes. (Fig. 2). Concentrations of initiators, emulsifier and suspension stabilizer similar to those used previously.

As shown in Figure 2, the reaction temperature has little effect on the course of the emulsion oligomerization in the first-kind emulsion using Potassium Persulfate (PP) and Hydrogen Peroxide (HP).

Changing the concentration of the initiator almost affects the molecular weight of the oligomer (Fig. 3). However, the effect of the initiator on the molecular weight of the product is significant: by using soluble initiators in a dispersion medium (water), oligomers with a higher molecular weight ($640\text{--}700$) are obtained than in the presence of an initiator soluble in the dispersed phase ($470\text{--}500$). For emulsion polymerization initiated by a water-soluble initiator, a slight influence of the temperature and initiator concentration on the free radical process is observed. This is probably due to its specific mechanism according to Smith-Ewartt and Medvedev's theory.

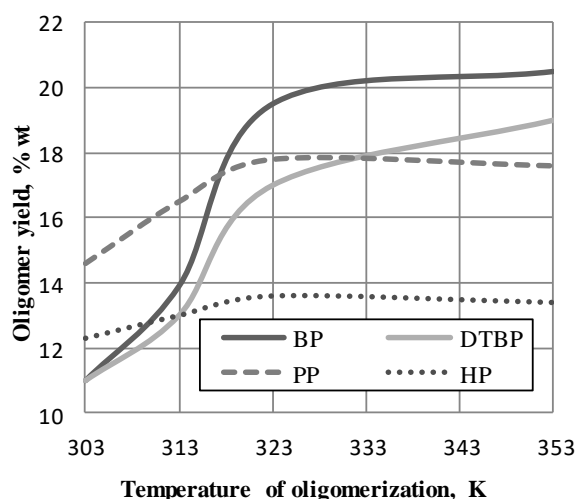


Fig. 2. Dependence of the oligomer yield on the reaction temperature ($\tau = 180 \text{ min}$; [fraction C9] : [water] = 1:2; $Re = 10120$; $C(\text{initiator}) = 1,0 \text{ wt.}$)

The dependence of the oligomer yield concentration initiators shown in Figure 3.

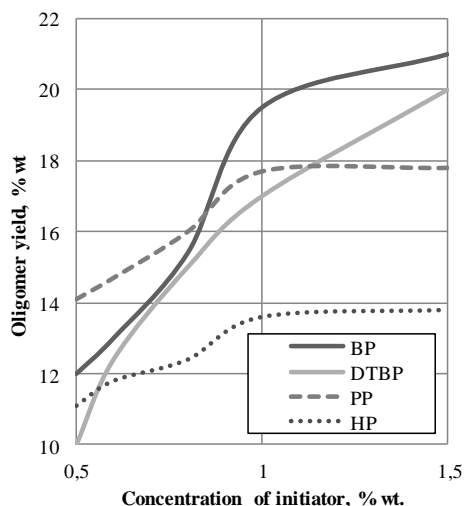


Fig. 3. Dependence of the oligomer yield on the concentration of initiator ($T = 323\text{ K}$; $\tau = 180\text{ min}$; [fraction C9] : [water] = 1:2; $Re = 10120$)

The yield, physical and chemical properties of oligomers per 180 minutes of synthesis are shown in Table.1.

The bromine number (degree of unsaturation) correlates with the yield of the oligomer. The bromine number decreases with increasing yield of oligomers.

The color index of the oligomers when using water-soluble initiators is low (20–40 mg I_2 / 100 ml by iodometric scale) and changes slightly with increasing initiator concentration (Table 1).

Hydrocarbon resins obtained by the emulsion oligomerization have a higher average molecular weight than the suspension one. Emulsion oligomerization obtained resin is characterizing by average molecular weight 650–700, suspension oligomerization resins ~500.

Table 1

Dependence of oligomer characteristics on reaction temperature and initiator concentration (the volume ratio [fraction C9] : [water] = 1:2; $Re = 10120$)

Characteristics	Emulsion oligomerization Initiator – Potassium Persulfate (PP) C (emulsifier E-30) = 0,7 % wt.			Suspension oligomerization Initiator – Benzoyl Peroxide (BP) C(suspension stabilizer) – 0,1 % wt.		
	0,5 % wt.	1,0 % wt.	1,5 % wt.	0,5 % wt.	1,0 % wt.	1,5 % wt.
303 K						
Bromine number, g Br_2 / 100 g	37,8	37,1	36,8	38,4	37,5	36,2
Softening point (temperature), K	348	358	357	358	352	350
Average molecular weight (cryoscopy)	650	690	670	500	495	490
Color index (by iodometric scale), mg I_2 /100 ml	20	20	20	20	20	20
313 K						
Bromine number, g Br_2 / 100 g	37,3	37,1	36,8	34,7	34,3	34,2
Softening point (temperature), K	360	358	357	358	352	354
Average molecular weight (cryoscopy)	700	690	670	500	490	490
Color index (by iodometric scale), mg I_2 /100 ml	20	20	20	20	30	20
323 K						
Bromine number, g Br_2 / 100 g	35,2	30,3	32,4	33,2	30,4	30,1
Softening point (temperature), K	348	358	354	345	350	352
Average molecular weight (cryoscopy)	650	690	685	470	490	500
Color index (by iodometric scale), mg I_2 /100 ml	20	20	30	20	30	30
353 K						
Bromine number, g Br_2 / 100 g	30,4	33,2	30,1	29,8	30,0	29,8
Softening point (temperature), K	355	347	348	359	358	355
Average molecular weight (cryoscopy)	680	640	650	500	495	490
Color index (by iodometric scale), mg I_2 /100 ml	20	40	30	20	20	30

The synthesized resins (oligomers) meet the requirements of TY Y 6-05743160.020–99 for resin oil-based synthetic paint.

Conclusions

Hydrocarbon resins were obtained by emulsion and suspension oligomerization. It was established that the obtained hydrocarbon resins contain mainly links of styrene and its derivatives. The influence of duration and temperature of oligomerization and concentration of initiators was investigated. Basic patterns of flow of suspension and emulsion oligomerization depending on the studied conditions was compared.

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ПОРІВНЯЛЬНЕ ДОСЛІДЖЕННЯ ОДЕРЖАННЯ ВУГЛЕВОДНЕВИХ СМОЛ МЕТОДОМ ЕМУЛЬСІЙНОЇ ТА СУСПЕНЗІЙНОЇ ОЛІГОМЕРИЗАЦІЇ ФРАКЦІЇ C9

Досліджено одержання вуглеводневих смол (коолігомерів) низькотемпературною дисперсійною коолігомеризацією вуглеводневої фракції C9 рідких продуктів піролізу дизельного палива. Цей спосіб дає змогу знизити температуру процесу. Синтез здійснювали емульсійною та суспензійною коолігомеризацією. Встановлено основні закономірності перебігу суспензійної та емульсійної олігомеризації вуглеводневої фракції C9. Досліджено вплив температури, концентрації ініціаторів та тривалості процесу на вихід та фізико-хімічні характеристики синтезованих олігомерів. Порівняно особливості перебігу емульсійної та суспензійної олігомеризації.

Ключові слова: олігомеризація, емульсія, суспензія, нафтополімерна смола, вуглеводнева смола, ініціатор, персульфат калію, пероксид бензоїлу.