The effect of the dispersion medium nature on the suspensive cooligomerization process of C_9 fraction

Oksana Orobchuk, Iryna Romankiv, Bohdan Polishchuk, Roman Subtelnyy

Department of Technology of organic products, Lviv Polytechnic National University,
UKRAINE, Lviv, S. Bandery street 12,
E-mail: or_oksana@ukr.net

Abstract – Processing by-products of ethylene production – liquid pyrolysis products is actual problem nowadays. Industrial methods of initiated cooligomerization of unsaturated hydrocarbon fraction C_9 have several disadvantages such as high temperature, duration of reaction, high performance color of oligomer .

To eliminate the difficulties carrying out of the process of cooligomerization in suspension is proposed to use precipitant as a dispersion medium for cooligomerization with components [fraction C_9] [dispersion medium] is suggested. A number of precipitants is as the dispersion medium ethanol, hexane and water is selected.

Influence of dispersion medium on the processs is investigated. The dependence of the yield and chemical characteristics of oligomer from nature of precipitant is shown. The optimal correlation of the components of the suspension is defined.

Key words: Suspension cooligomerization, hydrocarbons fraction, initiator, oligomer, ethanol, hexane.

I. Introduction

By-products of pyrolysis are produced during the production of ethylene, propylene, butylene and other precursors of organic synthesis. Depending on the composition of the feedstock particle liquid by liquid pyrolysis products can be 20-40%. The main part of these products is C_9 fraction. Today is the actual problem of rational use C_9 fraction. One way of recycling fraction is oligomerization to form oligomers which have wide scope.

In industrial environments cooligomerization of hydrocarbon fractions implement with the addition of a solution of oligomer catalyst (catalytic) and initiator (initiated). Hydrocarbon fraction is a mixture of saturated hydrocarbons in which monomer is dissolved (unsaturated hydrocarbons). The features of industrial methods of initiated oligomerization: high reaction temperature (453 ... 473 K), high reaction time (6 ... 8 hrs.), complexity of the selection of target products, high enough color (40 ... 100 mg I_2/100 ml) which significantly affects not only properties, but also the cost oligomer [1]. To eliminate the shortcomings inherent in the production process to carry out the process of oligomerization in suspension is proposed [2].

As a dispersion medium is water, oligomerization is carried out on temperatures up to 373 K. In this temperature range the main component that makes styrene resin is partially viniltoluols. Most of the saturated hydrocarbon fraction C_9 is xylenes and benzene derivatives. Thus we obtain a system of monomer – solvent. We get oligomer of large molecular weight hydrocarbons in solution, which do not participate in the reaction.

According to the theory of deposition polymers by Flory-Hahhens polymer can be precipitated out of solution of solvent and precipitant [3]. So assume that using precipitant as a dispersion medium will allow to identify oligomer for reaction oligomerization in suspension.

II. Carrying out the experiment

As raw material for oligomerization (dispersion phase) fraction C_9 of liquid by-products of pyrolysis diesel is used: density – 925 kg/m^3; bromine number – 68 g Br_2/100 g, molecular weight – 102, the content of unsaturated compounds to 45% including styrene 170,85% viniltoluols 6,99%, 18,00% dicyclopentadiene, indene 1,25 %. The dispersion medium is water, ethanol, hexane. Initiator of oligomerization is benzoyl peroxide (BOP) by technical production "MERCK" (Germany), containing the main product of at least 76,2%, temperature of thermolysis is 380HP. Suspension stabilizers are polyvinyl alcohol, polyethylene glycol.

Synthesis of oligomers by suspension oligomerization was carried out in three-neck flask with stirrer. Raw materials (C_9 fraction, and dispersion medium) proportions were served in a flask. The calculated amount of initiator solution and a suspension stabilizer were added in a flask. After loading the reagents rapidly stirred while heated to the desired temperature. The mixture was precipitated, filtered and dried in a vacuum oven at a temperature of 343 K. For oligomers yield (in terms of fraction C_9) and physic-chemical properties: unsaturation (bromine number), the rate of color iodometric scale (YMSH) molecular weight and softening temperature were determined.

III. Discussion of results

In industry the excretion of oligomer is performed by atmospheric and vacuum distillation. We propose to identify the product by precipitation.

According to the theory of deposition polymer Flory – Hahhens for polystyrene solvent –precipitant is proposes: benzene – methanol, toluene – methanol, toluene – petroleum ether , toluene – n- decane, toluene – ethanol, benzene – ethanol, butanol – ethanol, benzene – hexane; benzene – cyclohexane [3].

To determine the most effective precipitant of oligomers from the reaction mixture, of 1 ml oligomer solution was dissolved in benzene and added to 1 ml of precipitant after a determined period of time.

The precipitants we use are isopropyl alcohol, cyclohexanol, cyclohexane, hexane, n-butanol, isobutane, cyclohexanone, ethanol, petroleum ether, isoamyl alcohol, heptane.

The first portion of precipitant in samples of hexane, ethanol, petroleum ether, heptane, cyclohexanol, n-butanol, isobutanol, cyclohexanone solution dimmed. After

TABLE 1

THE EFFECT OF THE DISPERSION MEDIUM NATURE ON THE YIELD AND PHYSICAL AND CHEMICAL PARAMETERS OF THE KOOLIHOMERS

№	Ratio of the components	Value of phase	The yield, wt%.	Bromine number, g Br_2/100 g	Softening temperature, K	The average molecu-lar weight	Color, mg J_2/100 ml
1	[C_9 fraction]:[water]	1:1	9,8	44,9	334	680	20…30
		1:2	13,2	34,3	342	694	30…40
		1:3	10,1	40,7	339	687	30…40
2	[C_9fraction]:[ethanol]	1:1	13,9	37,6	318	379	20…30
		1:2	13,5	39,8	320	435	30…40
		1:3	11,1	41,0	328	396	30…40
3	[C_9fraction]:[hexane]	1:1	15,9	31,7	336	425	30…40
		1:2	13,8	29,4	343	430	30…40
		1:3	15,8	30,5	311	357	30…40

adding a second portion of precipitant oligomer released in the first four samples. After adding a third portion the results of the experiment were the same that in the previous case.

Based on the results we conducted series of experiments aimed at studying the process of suspensive oligomerization in which the dispersion medium is precipitant and water.

To determine the precipitant influence (ethanol and hexane) the yield and physic-chemical properties of oligomer researching of oligomerization of unsaturated hydrocarbons of C_9 fraction were held under conditions: temperature – 328 K, the experiment – 3 hours, the concentration of initiator benzoyl peroxide – 1.0 wt%., the ratio [C_9 fraction] ÷ [dispersion medium] – 1:1, 1:2 and 1:3, stabilizer suspension – polyethylene glycol (PEG-35), polyvinyl alcohol (0.1% by weight. faction C_9) (Table I).

The result of the reaction is a product with yield to 16% by weight, low in color, molecular weight – up to 700. Unsaturation of oligomers is correlated with its output. In three systems yield varies in the same range, but there is a different of physical and chemical properties oligomers. Using the dispersion medium of ethanol and hexane molecular weight of oligomers reduced by half in comparison with the product from the aqueous suspension.

The features of systems [fraction C_9]:[water] are phase separation on oligomer solution and water with dissolved stabilizer. Oligomer is isolated from oligomer solution by precipitation. Product is drained in a vacuum oven.

The system [fraction C_9]:[ethanol] after reaction of oligomerization we observe separation of the reaction mixture into phases: the upper layer (alcohol) and bottom (mostly oligomer). A part of precipitated oligomer with increasing amount of alcohol decreases sharply. The easiest way to distinguish oligomer in the system [fraction C_9]:[ethanol] = 1:1. In two other cases oligomer is isolated by distillation of the alcohol phase.

System [fraction C_9] [hexane] after the reaction of oligomerization is homogeneous. Deposition of oligomer is not observed. Oligomerization product was isolated by distillation.

Conclusion

The suspension method of process of oligomerization of unsaturated hydrocarbon of fraction C_9 in dispersive agent of different nature is conducted. The influence of the correlation of the components and the dispersion medium on the yield and physic-chemical parameters of oligomers is investigated. The oligomers obtained in an aqueous medium have satisfactory physical and chemical characteristics. The using of ethanol and hexane as precipitant is more reasonable at the stage of allocation of oligomers.

References

[1] R.O. Subtelnyy, O.M. Orobchuk, Y. A. Kurtash, B.O. Dzinyak, “Suspenzijna kooligomerizacija nenasichenih vuglevodniv frakciï C_9, inicijovana peroksidom benzoïlu“ [Suspension koolihomeryzation C_9 hydrocarbon fractions using isopropylbenzene hydro peroxide] // Visnik Nacional'nogo universitetu „L'vivs'ka politehnika”. Himija, tehnologija rechovin ta ïh zastosuvannja, no 726, pp. 187-189, 2012.

[2] R. A. Subtelnyy, O. M. Orobchuk, J. A. Kurtash, B.O. Dzinyak, “Suspenzionnaja kooligomerizacija pobochnyh produktov processa piroliza“ [The suspension kooligomerization by-products of the pyrolysis] *// "Neftegazopererabotka-2011": Materialy Mezhdunarodnoj nauchno-prakticheskoj konferencii,* Ufa, Russia, May 24-27, 2011. pp. 65.

[3] M. Kantov, “Frakcionirovanie polimerov“ [Polymer fractionation]. Moscow, USSR: Mir, p. 444, 1971.