Emulsion Co-oligomerization of Hydrocarbon Fraction C_9 With the Polyvinylchloride Production Waste as a Dispersion Medium

Oksana Orobchuk[1], Mykhailo Pidsadiuk[1], Roman Subtelnyi[1], Bohdan Dzinyak[1], Yliana Fuch[2]

1. Department of Technology of organic products, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12, E-mail: or_oksana@ukr.net
2. Fuchs Mastyla Ukraina LLC, UKRAINE, Lviv, T. Shevchenko street 327 A, E-mail:fuchs@fuchs-oil.com.ua

***Abstract* –The main raw materials for co-oligomers synthesis are waste and by-products of ethylene production, first of all □ a liquid pyrolysis products which contain aliphatic and aromatic hydrocarbons. The main part of these products is C_9 fraction. Emulsion co-oligomerization of hydrocarbon fraction C_9 allows for the maximum degree of processing liquid pyrolysis by-products, improve ecological production of ethylene, lower power inputs on the stage of the synthesis and release of co-oligomers compared to existing methods.**

The process of emulsion co-oligomerization with "emulsion water" (by-product of the suspension polyvinylchloride production) as a dispersion medium – have been investigated.

Keywords – emulsion co-oligomerization, C_9 fraction, initiator, co-oligomer, "emulsion water".

I. Introduction

In today's industrial development question of qualified use of by-products appears as ethylene production amount increases annually, leading to increasing of the amount of liquid by-products of pyrolysis (LBPP). The rational way of LBPP recycling is obtaining cooligomers on their basis. 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 oligomers cost.

Since the initiated co-oligomerization produces a cyclopentadiene-styrenic co-oligomers, a low-temperature technology of hydrocarbon fraction C_9 emulsion co-oligomerization of the is proposed. The peculiarity of co-oligomerization in an emulsion is the low temperature of the process (323 K), its insignificant duration (down to 3 hours), and the possibility of obtaining high-molecular weight and low color-coding co-oligomers. The emulsion mixture contains: a monomer (hydrocarbon fraction), water, emulsifier and initiator. The initiators are soluble both in the disperse phase (benzoyl peroxide) and in the dispersion medium (peroxides, persulfates). Emulsifiers are a variety of soaps: oleates, stearates, salt sulfocytes of paraffinic high boiling carbohydrates, castor oil. The concentration of the emulsifier in the system ranges from 0.1 to 2.0 wt% (relative to the dispersion medium). Emulsifiers quantitative of a certain nature depends on the value of their critical concentrations of micelles (CCM).

Suspension polyvinylchloride (PVC) manufactured in "Karpatnaftokhim" (Ukraine, Kalush city), a significant amount of "emulsion water" is obtained as a by-product. "Emulsion water" (EW) is a solution of residues of the emulsifier E-30 and a mixture of the initiator's decomposition products (bis (2-ethylhexyl) peroxydicarbonate, (Trigonox EHP-W60), dilauyl peroxide (Laurox W40), 2,4,4-trimethylpentyl 2- peroxidecanoate (Trigonox 423-W50)), in the amount of 0.1 – 0.2wt% (relative to the monomers weight).

The study of co-oligomers obtaining by emulsion co-oligomerisation with "emulsion water" as a dispersion medium is appropriate.

II. Experiments

As raw material for oligomerization (dispersion phase) fraction C_9 of liquid by-products of diesel pyrolysis is used: density – 936 kg/m^3; bromine number – 68 g Br_2/100 g, molecular weight – 102, the content of unsaturated compounds to 45% including styrene 17,85% viniltoluols 6,99%, 18,00% dicyclopentadiene, indene 1,25 %.

The initiator – water-soluble potassium persulfate (PC) with the content of the main product 99.0%. The emulsifier – E-30, a mixture of linear alkanesulfonates. The general formula R-SO3Na, where R – corresponds to a carbon chain with an average length of C_{15}.

Under the conditions of the process the main reactive monomers are styrene and its derivatives with a low boiling point. Selectivity observed in the reactivity of unsaturated hydrocarbons C_9 fraction as the maximum product yield is comparable with the amount of styrene in the raw material.

III. Results and Discussion

For the results comparison of "emulsion water" and tap water (TW) as a dispersion medium surface tension has been determined. The results of the study are shown in Fig.1.

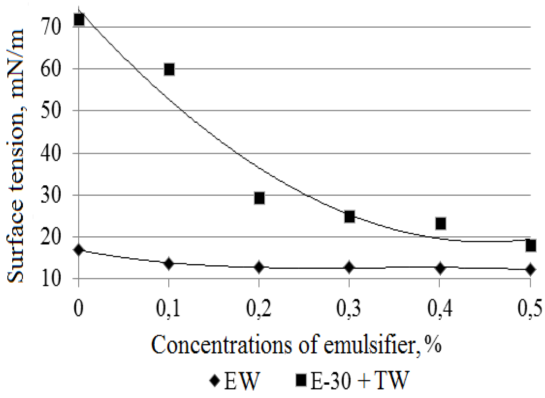

Fig.1 Isotherm of surface tension of "emulsion water" and tap water at different concentrations of emulsifier E-30.

It was determined that an increase in the amount of emulsifier E-30 in "emulsion water" only by 0.1% contributes to reducing the surface tension from 17.0 to 13.6 mN/m. An increase in the concentration of emulsifier above 0.1% has lesser effect on the surface tension.

"Emulsion water" is used as a dispersion medium in the process of the C_9 fraction unsaturated hydrocarbons emulsion co-oligomerization. Co-oligomers synthesis of was carried out under the following conditions: reaction temperature 323 K; volumetric phase ratio [fraction C_9]: [emulsion water] = 1: 1 ÷ 1: 3; reaction time 180 minutes.

For comparison, to the "emulsion water", an initiator of potassium persulfate was added in an amount of 0.1% by weight. (relative to the amount of fraction C_9), and an emulsifier E-30 with a concentration of 0.1% by weight (relative to the amount of water phase). The results of the research are shown in Fig.2.

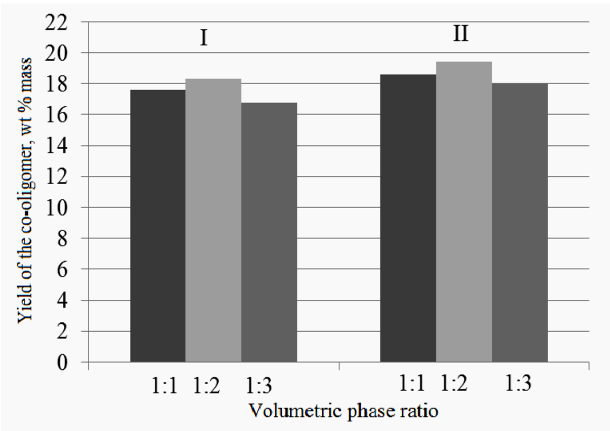

Fig.2 The volume phase ratio effect [fraction C_9] : [EW] on the yield of the co-oligomer
I – without emulsifier and initiator;
II – emulsifier (E – 30) = 0.1 wt%,initiator (PC) = 0.1 wt% mass, τ = 180 min)

The results of the study indicate that the use of "emulsion water" as a dispersion medium in the process of emulsion co-oligomerisation of fraction C_9 is appropriate. As a result, a co-oligomer with a maximum yield of 19.4% by weight was obtained. (with the ratio [fraction C_9] : [EW] = 1 : 2) and good parameters (molecular weight – 860, softening temperature – 350 K).

The maximum yield of the product (19.4% by weight) was obtained at the ratio [fraction C_9] : [EW] = 1 : 2 (concenation of the emulsifier and initiator 0.1% by weight), average molecular weight 860, softening temperature 350 K .

The results of the study are shown at Table 1.

The dependence of the product yield on the phase ratio for the dispersion medium of "emulsion water" is compatible with the dependence for co-oligomerization using as a dispersion medium of tap water.

TABLE 1

THE DEPENDENCE OF THE COOLIGOMER CHARACTERISTICS FROM THE EMULSION SYSTEMS COMPOSITION

Characteristics	[C_9 fraction]:[EW]			[C_9 fraction]:[EW] (C_I=0,1 wt%; $C_{E(E-30)}$=0,1wt%)		
Volumetric phase ratio	1:1	1:2	1:3	1:1	1:2	1:3
Bromine number, g Br_2/100 g	34,5	34,0	36,8	33,3	29,3	34,5
Softening temperature, K	346	348	344	348	350	349
The average molecular weight	755	760	755	810	860	815
Color, mg I_2/100 ml	40	40	40	40	40	40

Conclusion

The possibility of using – a by-product of the of suspension polyvinylchloride production – "emulsion water" (EW) for the synthesis of co-oligomers in the emulsion has been established. The results of the study indicate that the use of "emulsion water" as a dispersion medium in the process of emulsion co-oligomerisation of fraction C_9 is appropriate. As a result, a cooligomer with a maximum yield (19.4% by weight) was obtained at the ratio [fraction C_9] : [EW] – [1:2] and the following physical and chemical parameters: molecular weight – 860, softening temperature – 350 K. The proposed technology allows the rational use of petrochemical industrie by-products.

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