

The Effect of pH on Emulsion Oligomerization of C₉ Fraction in the Presence of an Anionic Emulsifier

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Abstract – Publication presents the results of research of emulsion oligomerization of mixture of unsaturated hydrocarbons of C₉ fraction of liquid diesel fuel pyrolysis by-products. An emulsion oligomerization of C₉ fraction in the presence of an anionic emulsifier and water-soluble initiator has been studied at various pH values.

Keywords - emulsion oligomerization, critical concentration of micelle formation, surface tension, oligomer, pH regulator.

Introduction

The production of olefins followed by a large number (30-35 % wt.) of liquid pyrolysis by-products. Liquid by-products (LBP) of pyrolysis are divided into separate fractions, for example: C₅, C₆₋₈, C₉. Based on LBP hydrocarbon fractions C₅ and C₉ respectively, are obtained aliphatic and aromatic (co)oligomers hydrocarbon/petroleum resins. Hydrocarbon resins have a wide range of applications. Particularly, hydrocarbon resins are used as film forming agents in lacquer-paint and anticorrosive coatings [1].

Such co-oligomers are obtained by of ionic, radical initiated and radical thermal co-oligomerization methods. Ion cooligomerization is carried out at low temperature. Its disadvantage is a high color index and an additional technological energy-consuming stage of the catalyst compartment from the reaction mixture. Cooligomerization using peroxide initiators (initiated co-oligomerization) is widely used in the industry. It allows obtaining cooligomers (hydrocarbon resins) high yield and good properties. The disadvantage of radical co-oligomerization is the high temperature of the process (453-473 K) and the complexity of the target product. The hydrocarbon resin is separated by distillation from a solution of unpolymerized fraction components. The aromatic hydrocarbon resins obtained on the basis of the C₉ fraction mainly consist of styrene-cyclopentadiene co-oligomers [1, 2].

The disadvantages of the industrial method of radical co-oligomerization of the C₉ fraction can be eliminated by using low-temperature dispersion co-oligomerization. Emulsion and suspension cooligomerization of hydrocarbons of fraction C₉ is considered [1, 2].

We propose to use 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. Emulsion cooligomerization is widely used in industry to make products that replace expensive and scarce materials of natural origin. This process is preferred because the reaction medium (which is usually water) makes it easier for promotes mixing, heat and mass transfer, and provides a safe process [2, 3].

Anionic surfactants have been used in various chemical fields. The ionic forms of their molecules also change with the pH of their aqueous solutions. Since the properties of the aqueous solution also change considerably with pH, accompanying the change of the ionic forms of the emulsifier. There have been many reports about the fundamental properties of their aqueous solutions depending on the pH values, e. g., micellization, surface tension, critical micelle concentration [4].

Emulsion polymerization is a method of polymerization of monomers dispersed in a dispersion medium to form a polymer/oligomer using inorganic initiator. As known, the system consists of dispersion phase (C₉ fraction), dispersion medium, a surfactant and a water-soluble initiator [3].

Experiments

The experiment was carried out at different values of reaction medium pH.

Composition of the reaction mixture of emulsion oligomerization:

- the dispersion medium - water;
- the dispersed phase – fraction C₉ of liquid pirolisis by-products (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 %.);
- water-soluble initiator - potassium peroxodisulfate (K₂S₂O₈) (1,0 %wt. calculated on the C₉ fraction);
- the emulsifier – E-30 a mixture of linear alkanesulfonates with length of the carbon chain - C₁₅ (0,7%wt. calculated on the dispersion medium);
- pH regulator – 40-% aqueous solutions of sodium hydroxide and hydrogen chloride.

Synthesis was carried out under the following conditions:

- temperature – 323 K;
- duration – 3 hours;
- volume ratio [fraction C₉]: [water] = [1 : 2];
- mixing intensity – Re = 10120.
- pH medium values – 0,5-12,0

The emulsion oligomerization of the C₉ fraction was carried out in a three-necked flask equipped with a rotary stirrer. The flask heating was carried out on a water bath. After loading, the reagents were vigorously stirred with a rotary stirrer and simultaneously heated to a temperature of 323 K for 3 hours.

The resulting mixture was separated by centrifuge (4000 rpm). As a result, a lower layer - an oligomer was separated. The oligomer was further dried. The liquid phase contains water and unreacted fraction C₉ hydrocarbons in its composition. If necessary, the liquid phase after centrifugation was separated by atmospheric distillation (pressure 0,11 MPa, cube temperature 453 K) and vacuum distillation (residual pressure 3 - 4 hPa, temperature 450 K). In this case, the oligomer was obtained in the cube, which was not separated by centrifugation.

Results and Discussion

To investigate the effect of reaction medium pH on emulsion oligomerization we define oligomers yield for different medium pH values. The pH values 2,8 corresponds to the reaction mixture (fraction C₉, water, initiator, emulsifier) without the addition of pH regulators.

Chromatographic analysis revealed that at this stage, the styrene and derivatives 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.

The dependence of the medium pH values on the yield of oligomers is shown on Fig. 1.

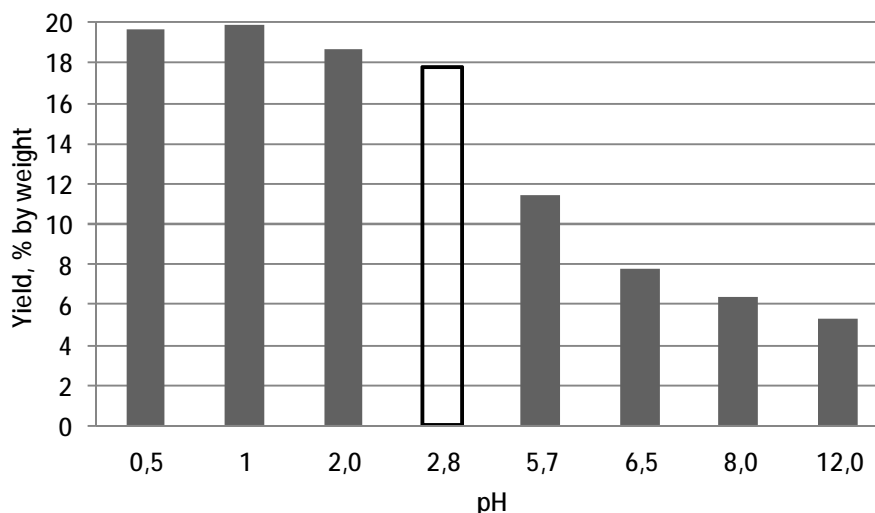


Fig.1. The effect of reaction medium pH values on the oligomer (hydrocarbon resin) yield in emulsion oligomerization.

As shown in Fig. 1, the maximum value of the oligomers yield is achieved in an acidic medium (pH = 1,0) and equals 19,9% by weight. Obviously, the reduction of pH to 0.5 has no significant effect on oligomer yield. With an increase in the pH value from 0,5 to 12,0, the yield of the oligomer decreases from 19,9 to 5,3% by weight. An emulsion oligomerization of the reaction mixture without the addition of pH regulators produced an oligomer with a yield of 17,8% by weight. Thus, we can conclude that increasing the pH value leads to increasing the yield of oligomers.

The emulsion oligomerization of the fraction C₉ hydrocarbons corresponds to the known theoretical laws [5, 6].

Physical and chemical characteristics of hydrocarbon resins (Table 1) obtained by emulsion oligomerization depend on the pH of the reaction mixture medium.

Table 1

Physical and chemical properties of (co)oligomers

Characteristic	pH							
	0,5	1,0	2,0	2,8	5,7	6,5	8,0	12,0
Bromine number, g Br ₂ / 100 g	23,1	23,0	24,7	30,3	34,8	35,9	39,7	42,0
Softening point, K	358	358	356	351	344	349	355	350
Color by iodometric scale, mg I ₂ /100 ml	80	60-80	30-40	30	40	40-60	40-60	60

As can be seen from the above results (Table 1), the bromine number (unsaturated value) correlates with the output of the polymer. The bromine number decreases with an increase in the of the oligomers yield. The color index of the oligomers (on the iodometric scale) increases with the addition of pH regulators. Color index increases from 30 mg I₂/100 ml (pH = 2,8 - oligomerization without the addition of pH regulators) to 80 mg I₂/100 ml (pH = 0,5). A high color index is undesirable for hydrocarbon resins (restricts their use in acquer-paint and anticorrosive coatings).

Infrared spectroscopy of the products obtained at the C₉ fraction emulsion oligomerization was carried out. Intense absorption bands of valent C-H-aromatic and CH₃-oscillations (region 2950-2916 cm⁻¹). Intense peaks in the region 1440-1600 cm⁻¹ (valence fluctuations of the

aromatic nucleus) indicate the presence of benzene nuclei in the structure of the co-oligomer, as well as fragments of the peroxide initiator. The high intensity of absorption bands in the region of 1000 - 1175 cm^{-1} indicates the presence of 1,2-, 1,4- and 1,2,4-substituted compounds. In the region of 680 - 800 cm^{-1} , less intensive bands of monosubstituted aromatic compounds and intense 1,2-substituted compounds (724 cm^{-1}) are observed.

There is a positive effect of acidic pH values on the oligomer yield. The process of emulsion oligomerization is influenced by many factors. One of the most important factors is emulsifier concentration. The critical micelle concentration is a relatively narrow concentration range, which indicates the limit below which no micelles are and above which almost all the surfactant, which is added to the solution, forms micelles. Evidence of surfactant micelles formation is bending dependencies property - concentration. The pH regulator (chloride acid) is an electrolyte. It is generally known that electrolytes reduce the critical micelle concentration.

Conclusion

The effect of medium pH on the process of emulsion oligomerization (oligomers yield) has been investigated. The optimum pH value has been determined. It is established that in the acidic medium the oligomer yield is growing. The resulting oligomers have a higher color index and softening temperature, the bromine number is not depending of medium pH.

References

- [1] R. O. Subtelnyi, O. M. Orobchuk, O. R. Dresher, B. O. Dziniak. "Cyclopentadiene oligomer synthesis based on C₉ fraction of liquid pyrolysis products". *Visnyk Natsionalnoho universytetu „Lvivska politehnika”. Khimiia, tekhnolohiia rehovyn ta yikh zastosuvannia*, vol. 886, pp. 102–106, 2018.
- [2] R. O. Subtelnyy, U. V. Fuch, B. O. Dzinyak. "Emulsion cooligomerization of mixture of unsaturated hydrocarbons of fraction C₉ using of potassium persulfate", *Actual problems of chemistry and technology of organic substances (APCTOS)*, Lviv, 2012, p. T24.
- [3] G. Odian. "*Principles of Polymerization*". New-York, 2004, 839 p.
- [4] K. Kato, H. Kondo, M. Takeda. "The effect of pH on emulsion polymerization of styrene in the presence of an amphoteric emulsifier". *Colloid and Polymer Science*, vol. 265 (11), pp. 950–956, 1987.
- [5] S. Grant T.D., V. Gerald A., R. Alfred. "Practical aspects of the emulsifier-free emulsion polymerization of styrene". *European Polymer Journal*, vol. 30 (2), pp. 179–183, 1994.
- [6] J. Zeaiter, J. A. Romagnoli, G.W. Barton, V. G. Gomes, B. S. Hawkett¹, R. G. Gilbert. "Operation of semi-batch emulsion polymerisation reactors: Modelling, validation and effect of operating conditions". *Chemical Engineering Science*, pp. 2955–2969, 2002.