The effect of surface tension of dispersion medium on the process of emulsion cooligomerization of C_9 fraction

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***Abstract* – This publication presents the results of research of emulsion cooligomerization of mixture of unsaturated hydrocarbons of C9 fraction from liquid products after diesel pyrolysis. This mixture of hydrocarbons is a by-product of the olefins production. This is one of the possible options to reduce the process temperature and duration of reaction, and hence energy consumption.**

The effect of surface tension on the process was investigated. The dependence of the concentration of emulsifier E-30 on the surface tension of different dispersive media is shown. Optimal critical concentration of micelle formation and the best dispersion medium for the process are determined.

These results are of practical interest in refining technology of diesel fuel pyrolysis by-products.

Key words: emulsion cooligomerization, critical concentration of micelle formation, surface tension, cooligomer, ethanol, heptane.

I. Introduction

As known the production of olefins followed by a large number (35%) of liquid pyrolysis products, which include the C_9 fraction. These products may be used to obtain cooligomers – petroleum resins [1].

In this paper we propose to use emulsion method of cooligomerization of unsaturated hydrocarbon of C_9 fraction of diesel pyrolysis liquid products. This method can significantly reduce the process temperature and reaction time compared to the industrial methods of cooligomers 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].

Emulsion polymerization is a method of polymerization of monomers dispersed in a dispersion medium to form a polymer using inorganic initiator. As known, the system consists of dispersion phase (C_9 fraction), dispersion medium, a surfactant and a water-soluble initiator [3,4].

The process of emulsion cooligomerization is influenced by many factors. One of the most important factors is emulsifier concentration. Therefore, our goal is to determine the critical concentration of micelle formation for different substances, namely heptane, ethanol, water.

The critical concentration of micelle formation (CCMF) 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. As the properties of the solution can be used specific and molar conductivity, surface tension, turbidity, osmotic pressure, refractive index, and others. There are dozens of famous methods for determining the CCMF, and for certain surfactant various methods give approximately the same value of CCMF in case of their skillful application. In this case, we determine the surface tension by method of liquid droplets to study the influence of surface tension on the emulsion cooligomerization [5].

II. Experiments

The experiment was carried out at different concentrations of surfactant (emulsifier E-30) for different dispersion media, namely, heptane, ethanol, water.

Determination of surface tension of pure water and aqueous solutions of surfactants (at room temperature), is carried out by the method which is based on weighing drops.

Then we carried out emulsion cooligomerization of unsaturated hydrocarbon mixture of C_9 fraction of diesel pyrolysis liquid products. We used C_9 fraction as the raw material.

TABLE 1

C_9 FRACTION CHARACHTERISTIC

density	925 kg/m^3
bromine number	95 g Br_2/100 g
molar weight	102
unsaturated compounds content	to 45 %
especially:	
-sthyrol	17,85 %,
-vinyltholuol	6,99 %
-dicyclopentadiene	18,00 %
-indene	1,25 %

The dispersion medium is water, heptane, or ethanol. As the initiator we used potassium persulfate – $K_2S_2O_8$. Emulsifier E-30 is a mixture of linear alkanesulfonates with length of the carbon chain – C_{15}.

Cooligomerization of unsaturated hydrocarbons was carried out in the three-neck flask to which was loaded raw materials (C_9 fraction, and dispersion medium), initiator and emulsifier. The process was carried out with continuous stirring and heating (process temperature is 323K).

III. Results and Discussion

To investigate the effect of surface tension on emulsion ooligomerization we define CCMF for different dispersion media, namely, heptane, ethanol, water.

The dependence of the surface tension of different dispersion media on the concentration of emulsifier (E-30) is shown on Fig. 1.

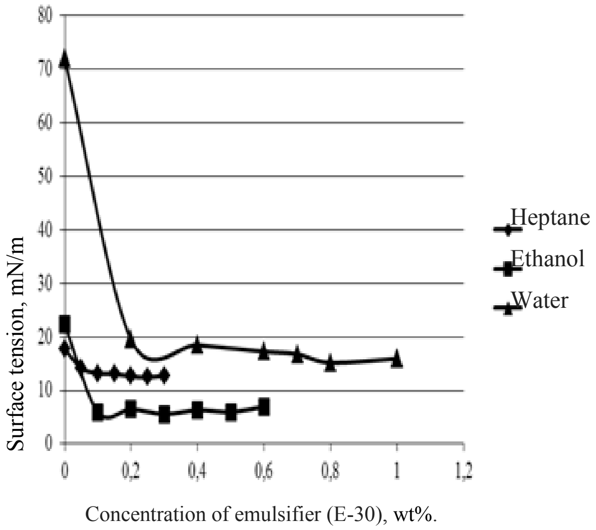

Fig. 1. The influence of emulsifier concentration of E-30 on the surface tension of different dispersive media

As shown in Fig. 1, the critical concentration for micelle formation for heptane is reached at emulsifier E-30 concentration 0.1 wt %, for ethanol – 0.1 wt %, for water – 0.2 % by weight. Also in this case there is a sharp decrease in surface tension for the dispersion medium heptane, ethanol, water, respectively: 17,8 ÷ 12,4; 22,3 ÷ 5,9; 72,0 ÷ 19,5 mN/m. The variation of surface tension of ethanol and water in the presence of surfactants coincides with the classical theoretical concepts, but in the case of heptane, the character of the curve has some differences, probably due to its nature as the surface tension is slightly dependent on the surfactant concentration. Thus, we can assume that the most suitable dispersion medium for the process of emulsion cooligomerization is heptane and ethanol as to reduce their surface tension the surfactant amount needed is fewer (only 0.1 % wt.).

Obviously, the further increase of the surfactant amount has no significant effect on surface tension.

TABLE 2

THE EFFECT OF SURFACE TENSION OF DISPERSION MEDIUM ON THE PROCESS OF EMULSION COOLIGOMERIZATION

Dispersive medium	Emulsifier concentration %	Surface tension, mN/m	Cooligomers yield, %
Water	0.2	19.48	15.9
	0.7	16.78	15.8
Heptane	0.2	12.64	10,6
Ethanol	0.2	6.48	8.7

The next step was to carry out emulsion cooligomerization in the presence of following dispersive medium: ethanol, heptane, water, with a constant emulsifier concentration. The results are shown in Table 2.

The maximum values of surface tension solution of the dispersion medium and emulsifier yield is also the highest,that show from the table. So the impact on the course of the reaction koolihomeryzation have ethanol and heptane.

For comparison process was also carried out with higher emulsifier concentration of 0.7 % by weight, and water was used as a dispersion medium, the yield of cooligomer is 15.00 %. Thus, we can conclude that increasing the emulsifier concentration leads to increasing surface tension and reducing the yield of cooligomer. This was most clearly seen in the water, therefore, to use a significant amount of emulsifier is inexpedient.

Conclusion

The effect of surface tension on the process of emulsion cooligomerization was investigated. The optimum critical concentration of micelle formation for different dispersive media was determined. The method of emulsion cooligomerization process of unsaturated hydrocarbon of C_9 fraction was investigated in dispersive media of different nature. The effect of emulsifier concentration on the cooligomers yield was determined.

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