

Catalytic Cooligomerization of Terpenic and Aromatic Hydrocarbons

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Abstract – Main regularities of cationic cooligomerization of terpenic hydrocarbons, being contained in turpentine, and aromatic hydrocarbons, being contained in C₉ fraction of diesel fuel pyrolysis liquid products, have been found out. Homogeneous complex of aluminium chloride with ethyl acetate in organic solvent (xylene) has been suggested as a new efficient catalyst of the process.

Keywords – catalytic cooligomerization, C₉ fraction, turpentine, hydrocarbon resins, polyterpenic resins, catalytical complex.

I. Introduction

Turpentine is second after rosin most important product of wood chemistry. Its world production capacity is estimated to be 280 thousand ton per year. That is why development of modern wood chemistry is inseparably linked with the development of new methods of turpentine processing. Production of cooligomers of monoterpenic hydrocarbons with various monomers is one of promising directions of turpentine use.

The C₉ fraction of liquid pyrolysis products is a by-product of ethylene production. It is a mixture of saturated and unsaturated hydrocarbons mostly of aromatic nature.

Presence of double bonds in structures of aromatic and monoterpenic hydrocarbons, as well as bridge cyclic fragments in monoterpenic hydrocarbons determines their chemical reactivity and, in particular, polymerizability.

II. Experimental

In present study the C₉ fraction of diesel fuel pyrolysis liquid products was used as a source of aromatic hydrocarbons. Main polymerizable hydrocarbons of the fraction include: styrene (18.93 wt.%), allylbenzene (0.86 wt.%), α -methylstyrene (1.97 wt.%), vinyltoluenes (8.13 wt.%), dicyclopentadiene (17.78 wt.%), indene (1.93 wt.%).

The turpentine, obtained from gallipot by steam distillation or vacuum distillation, was used as a source of terpenic hydrocarbons. This type of turpentine has been chosen, because it is the best raw material among the other industrial types of turpentine (steam, extraction, dry distillation, sulphate) due to the high content of unsaturated terpenic monomers, namely α -pinene (60-70 wt.%) and Δ^3 -carene (10-18 wt.%).

The AlCl₃/ethyl acetate/xylene liquid catalytic complex with the components molar ratio AlCl₃/EA/xylene = 1:0.5:2 was used as a catalyst.

Cooligomerization of the aromatic and terpenic monomers was carried out in four-necked thermally stabilized reactor fitted with stirrer, thermometer, dropping funnel, backflow condenser, sampling valve and barboter of inert gas – argon. The process temperature was 343 K, duration – 3 h., turpentine/C₉ fraction ratio – 10:90, the catalyst concentration ranged from 1.0 to 3.0 wt.% (calculated in terms of AlCl₃ per initial feedstock). After finishing the cooligomerization the catalytic complex was neutralized and removed from the reaction mixture (cooligomerizate). Unreacted hydrocarbons were removed by vacuum stripping of the cooligomerizate.

III. Results and Discussion

The catalytic complex concentration (C_{cat.}) influence on the yield and physico-chemical properties of aromatic-terpenic resins (ATR) were studied at turpentine/C₉ fraction ratio equal to 10:90. The results obtained are given in Fig. 1-3.

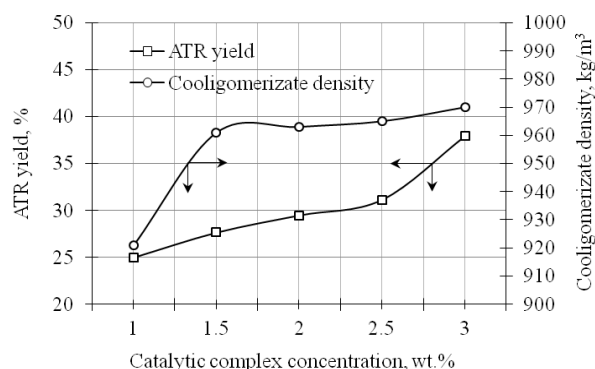


Fig. 1. The ATR yield and the cooligomerizate density dependence on the catalytic complex concentration

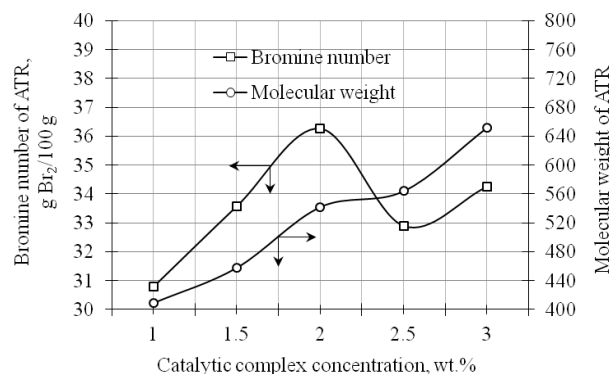


Fig. 2. The ATR bromine number and molecular weight dependence on the catalytic complex concentration

The experimental data show that C_{cat.} increase from 1.0 to 3.0 wt.% has a positive impact on cooligomerization process, because the cooligomerizate density increases (from 921 kg/m³ to 970 kg/m³) and the ATR yield increases (from 25 % to 38 %) as well (Fig. 1). The result is expected, because catalyst amount increase promotes initiation and propagation of polymer chain. This fact also explains the increase of molecular weight in the range from 409 to 652 at the catalyst concentration range from

1.0 to 2.0 wt.% (Fig. 2). Bromine number of ATR increase from 29 g Br₂/100 g to 36 g Br₂/100 g when the catalyst concentration increases from 1.0 to 2.0 wt.%, but further increase of the catalyst concentration results in bromine number decrease by 3 g Br₂/100 g on the average at the catalyst concentration 2.5 wt.% and 3.0 wt.%.

As we can see from the results, when raising the catalytic complex concentration, the ATR molecular weight and the cooligomerizate density increase considerably. However, the product yield increases slightly, when raising the catalyst concentration.

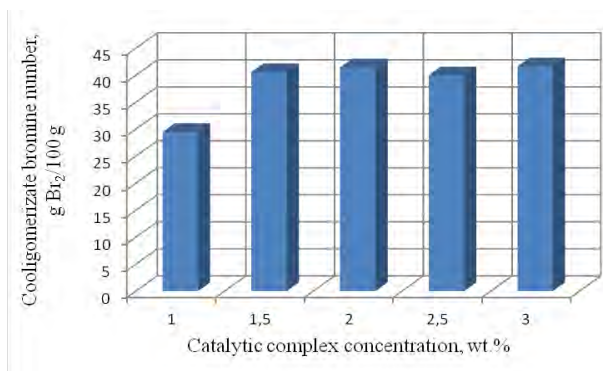


Fig. 3. The cooligomerizate bromine number dependence on the catalytic complex concentration

Using of high concentration of aluminium chloride in the reaction mixture is unfavourable, because it raises corrosion activity of the reaction mixture. Economically, raising of the catalytic complex concentration over 3 wt.% (in terms of aluminium chloride) is also unreasonable.

Conclusion

Turpentine and C₉ fraction are efficient and affordable sources of aromatic and terpenic monomers for catalytic cooligomerization processes.

Based on the results obtained we can conclude that the catalytic complex optimal concentration is 3 wt.% (in terms of aluminium chloride). The resin obtained has the following characteristics: yield – 41.1 %; bromine number – 21.3 g Br₂/100 g; molecular weight – 1124; colour – 200 mg I₂/100 cm³; softening point – 366 K.

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