Production of plasticizers from waste alcohol production

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Abstract – The aim of this work was to study the possibility of recycling disposal alcohol production by its processing in order to obtain valuable products, namely plasticizers.

Key words – plasticizer, fusel, esterification reaction.

I. Introduction

Alcohol industry of Ukraine is one of the most developed sectors of the food industry. Raw alcohol, which, is obtained after the distillation fusel, contains a lot of impurities, different in chemical nature and composition. The total content of impurities typically doesn't exceed than 0.7% weight of ethanol. However, today, have not solved the problem of recycling such products as fusel oil production. Every year in Ukraine in the production of alcohol it is produced about 2 thousand tons.

II. Page Setup

The aim of this work was recycling the alcohol production to produce plasticizers.

To do this, received a mixture of esters based fusel oil adulterances methodby acid-catalytic esterification. As the catalyst used concentrated sulfuric and phosphate acid in amounts of 1.5% and 2.5% according to weight of phthalic anhydride. Because the reaction of the esterification is reversed, it should be performed with a small excess of one of the initial reagents (fusel oils) and selection of formed water. So, when in the literature review was found an optimal molar ratio of alcohols to phthalic anhydride, which is 2.2: 1. Proceeding from the fusel oil was found necessary amount of phthalic anhydride and catalyst. Also added 10 g of benzene as azeotropic supplement.

There has been constant heating of the reaction mass to support its boiling point of distillation azeotrope benzene -water. This vapor evaporated, appeared in the back of the fridge, where condensed and sent to the Dean-Stark attachment from which the organic fraction returned back to the reactor.

Stopping the allocation of water from the reaction mixture and its accumulation in the attachment Dean-Stark, indicating complete esterification reaction. The duration of the process depended on the nature and quantity of catalyst.

Purification of the reaction mixture is performed as follows. First, in a dividing funnel, the reaction mixture was washed with 10% sodium carbonate solution to bring the product to a neutral environment. This was happened bundles in organic and aqueous fractions. The aqueous fraction was poured and additional dried by organic extra burning $MgSO_4$, then spent filtering. The resulting product was subjected to vacuum distillation, during which distilled off remains unreacted alcohols. The temperature of the vapor varies in the range 56-59 ^oC when vacuum is 0.82 atm. Product analysis is carried out by means of chromatography and infrared spectroscopy. To determine the plasticizing properties of the product was conducted the determination of melt flow index (MFI) and study the thermo-mechanical properties of PVC with the addition of a plasticizer for the resulting product quality and without it. Thermomechanical studies were performed on the instrument FVD R7 / 90.

III. Page Setup

Esterification reaction is carried out in a reactor equipped with the attachment Dean-Stark reflux.

As the catalyst used concentrated H_2SO_4 and H_3PO_4 in amounts of 1.5% and 1.5%, respectively 2.5% according to the mass of phthalic anhydride.

Observated accumulation of water in the Dean-Stark attachment is shown in Figure 1. Thus, when used as a catalyst H_2SO_4 is observed more intense accumulation of water than using H_3PO_4, indicating greater speed of reaction. The main disadvantage of sulfuric acid was a significant burnt down of phthalic anhydride.

As a result of chromatographic analysis chromatogram obtained the product (Figure 2). It recorded four peaks which are probably correspond to the phthalic esters.

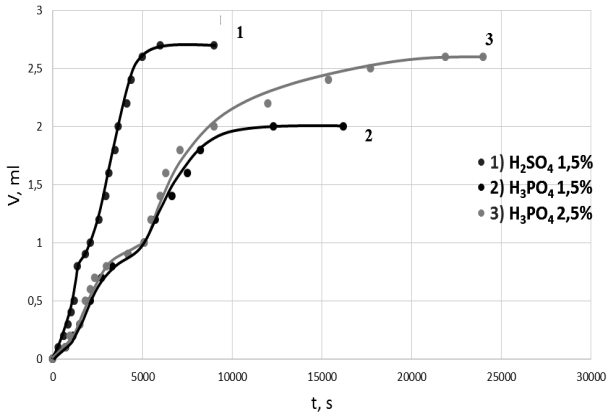


Fig. 1. Kinetics of accumulation of water fraction

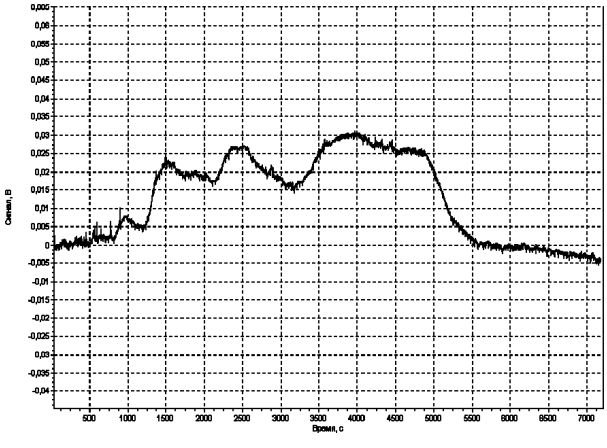


Fig. 2. chromatogram product

An infrared spectroscopy of the product, indicating the presence of ester groups (1740,1284,1124 sm^{-1}), that the presence of phthalic acid esters.

IR spectrogram is shown in Figure 3.

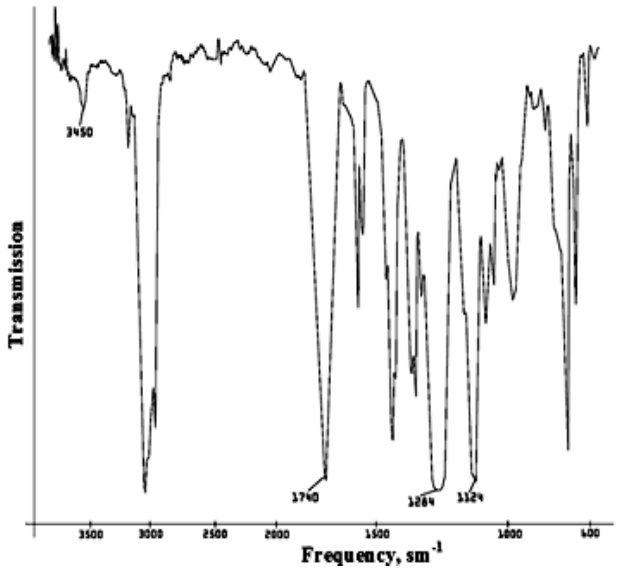


Fig. 3. IR spectrogram product

To identify plasticizing properties of the product is used plastomir extrusion type "YYRT." It has been experimentally determined the best conditions of the process: temperature 170 and 190°C and loads 14.95 kg and 11 kg. The results are shown in tabl.1

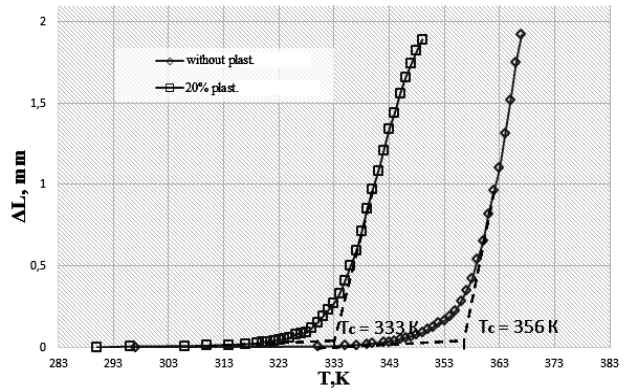
According to these results when adding the mixture of esters are observed an increase of 14 (at 20%) and 10.5 (at 10%) times the flow rate, which indicates a significant plasticizing properties of the product.

TABLE 1

RESULTS OF THE DETERMINATION OF THE MFI

Sample	Темр., °C	MFI, g/10m
PVC	170	0,22
PVC + plasticizer (20%)		3,078
PVC	190	0,123
PVC + plasticizer (10%)		1,3

Thermomechanical behavior of polymeric materials is an important characteristic that determines the conditions of their use. For comparison studies following samples were taken: 1) PVC plasticizer content of 20% (temperature plasticizing 170°C), 2) PVC plasticizer content of 10% (temperature plasticizing 190 °C); 3) PVC without plasticizer (temperature plasticizing and 190°C 170). The research results are presented in Fig. 4 and Fig.5.



Fi. 4. Thermomechanical curves PVC plasticizer content of 20% and without it, at received plasticizing 170°C

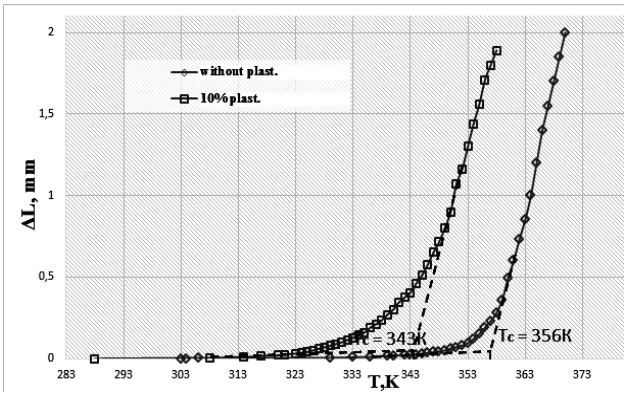


Fig. 5. Thermomechanical curves PVC plasticizer content of 10% and without it, at received plasticizing 190°C

As seen from thermomechanical curves obtained with increasing content of plasticizer in PVC increases its plasticity. So, determined glass transition temperature of PVC without plasticizer was 356K, using 10% plasticizer - 343K at 20% - 333K, indicating a distinct plasticizing properties of our product.

Conclusion

Thus, as a result of the research conducted the possibility of using fusel oil for the synthesis of plasticizers based on esters of phthalic acid. The features esterification process fusel oils and impact of the catalysts on its course. The method of gas-liquid chromatography and infrared spectroscopy determined presence in the obtained product containing phthalates alcohol fusel oil. The study of the glass transition temperature and melt flow index set plasticizing properties of the product. Thus, the use of the obtained plasticizer in an amount of 20% by weight. mixtures glass transition temperature decreased by 23°C and as an indicator of the melt flow rate increased by 13 times.