

## ESTERIFICATION OF TRIMETHYLOLPROPANE WITH FATTY ACIDS

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Esters of polyhydric alcohols are very promising components for synthetic lubricating oils for a wide temperature range. They have good viscosity characteristics at low temperatures, a high viscosity index, good lubricating ability and high thermal stability [1-6].

Various catalysts are used to prepare such esters: strong inorganic acids; aromatic acids, for example, p-toluenesulfonic acid; metal oxides; sodium bisulfate, etc. [7].

Since the existing literature was insufficient to choose a catalyst for the esterification of trimethylolpropane with fatty acids, it seemed expedient to us to carry out a comparative evaluation of the activity of some catalysts.

The esterification of trimethylolpropane was carried out in a four-neck round-bottom flask with a Dean and Stark water separator in a nitrogen stream at 110-120°C; the mixture was dissolved up in toluene as an azeotroping agent. The trimethylolpropane was esterified with iso- and n-valeric acids in two stages. The constants of the starting materials were close to the recorded literature data. Initially, isovaleric acid was introduced into the reaction in the amount necessary to esterify one OH group of the trihydric alcohol, and then n-valeric acid was added in an amount sufficient for two OH groups. The end of the reaction was determined from the amount of water separated and from the acid number. At the end of the process, the product was washed with hot water, a 10% alkali solution, and again with water to a neutral reaction with phenolphthalein. After the esterification product had been dried over freshly ignited sodium sulfate, the toluene was stripped off in a nitrogen stream. The "crude ester" obtained was purified with decolorizing carbon, brand "A", taken in an amount of 10% on the weight of ester, with stirring over a four-hour period at 90°C, after which it was distilled in vacuum at 1-2 mm.

For the ester of trimethylolpropane with iso- and n-valeric acids in the ratio 1:2, the following physico-chemical properties were found: b.p. 180-185°/2 mm; ester number, 436; acid number, 0; density,  $\rho_4^{20}$ , = 0.9930; refractive index,  $n_d^{20}$ , = 1.4490; solidification point, below -70°C; kinematic viscosity,  $\nu_{100}$  = 3.25 cc,  $\nu_{50}$  = 8.0 cc,  $\nu_{40}$  = 1130 cc.

We studied the catalytic activity of a number of catalysts; sulfuric or phosphoric acids, p-toluenesulfonic acid, aluminum oxide, zinc oxide, phosphorus pentoxide, sodium bisulfate, and cationic ion exchange resin KU-2. The zinc and aluminum oxides were preliminarily ignited in a muffle at 400°C for 5 hrs.

The duration of the esterification reaction served as a criterion of the effectiveness of catalyst action.

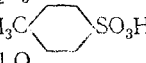
The sulfuric, phosphoric and p-toluenesulfonic acids were used in an amount of 1-2%; the zinc and aluminum oxides, in an amount of 10%; the cation exchange resin and sodium bisulfate, in an amount of 7%, based on total charge of reagents.

The duration of esterification in presence of various catalysts is shown in Table 1.

From the data presented, it follows that at 110-120°C sodium bisulfate is the most effective catalyst. This compound does not dissolve in the reaction mixture; in this connection the necessity for an alkaline wash and neutralization of the ester obtained disappears. At the end of the reaction the toluene solution was filtered to remove catalyst, the solvent was stripped, and the residue was distilled under vacuum (1-2 mm Hg).

We have established that an increase in molecular weight of the acid does not exert an effect on the length of the esterification process; thus, reactions with caproic, enanthic, caprylic, and pelargonic acids in the presence of 3% sodium bisulfate were finished after 3-5 hrs; the yields of esters were 90-94%.

TABLE 1. Effect of Catalyst on Length of Process of Esterifying Trimethylolpropane with Iso- and n-valeric Acids. Experimental Conditions: 110-120°C, Nitrogen Medium

Catalyst	Amt. of catalyst, % of charge	Duration of esterification, hrs.	Yield of crude ester, wt. %
H <sub>2</sub> SO <sub>4</sub> *	1	60	83 †
H <sub>3</sub> PO <sub>4</sub>	1,67	23	87
P <sub>2</sub> O <sub>5</sub>	1	26	90
H <sub>3</sub> C  SO <sub>3</sub> H	2	24	77
Al <sub>2</sub> O <sub>3</sub>	10	90	70
ZnO	10	60	70
KU-2	7	10	81
NaHSO <sub>4</sub>	7	2	85

\* Density 1,84.

† The esterification product obtained was dark-colored.

TABLE 3. Effect of Temperature on Length of Esterification of Trimethylolpropane with Iso- and n-valeric Acids

Azeotroping agent	Reaction temperature, °C	Length of esterification, hrs	Yield of ester, wt. %
NaHSO <sub>4</sub> catalyst			
Toluene	110—120	2	84,5
Xylene	130—140	2	85,0
Cumene	150—160	2	83,8
H <sub>2</sub> SO <sub>4</sub> catalyst			
Toluene	110—120	60	78,0
Xylene	130—140	10	69,1
Cumene	150—160	1	65,7

the temperature strongly reduces the reaction time. Thus, in the esterification of trimethylolpropane with fatty acids in the presence of 1% sulfuric acid, an increase in reaction temperature from 110 to 160°C reduces the duration of the process from 60 hrs to 1 h.

However, side reactions are intensified thereupon; these lead to resin formation, which reduces the yield of ester to 65.7% (see Table 3).

## CONCLUSIONS

1. It has been shown that sodium bisulfate in an amount of 3-5% significantly shortens the reaction time compared with the most widely used catalysts in esterification of trimethylolpropane with fatty acids; it simplifies subsequent treatment of the reaction mixture, and increases the yield of ester. Changing the process temperature with the range 110-160°C does not affect the reaction time; therefore esterification with a yield of ester above 90% can be conducted at 110-120°C.

2. It has been shown that in the presence of sulfuric acid, on raising the experimental temperature from 110 to 160°C, the duration of the process is cut from 60 hrs to 1 h, but the yield of ester decreases significantly.

TABLE 2. Effect of Amount of NaHSO<sub>4</sub> Catalyst on Length of Esterification of Trimethylolpropane with Caprylic Acid. Experimental Conditions: 110-120°C, Nitrogen Medium

Amt. of catalyst, % of charge	Duration of esterification, hrs.	Acid no. at end of esterification, mg KOH/g		Yield of ester, wt. %
		determine	calc.	
0,5	11	50,0	17,5	65
1,0	6	20,0	17,5	83
3,0	3	18,1	17,5	87
5,0	2,5	18,0	17,5	91

Experiments on a study of the activity of sodium bisulfate as a catalyst were conducted in the case of esterification of trimethylolpropane with n-caprylic acid. When the catalyst was increased from 0.5 to 5% (Table 2), the duration of the process was cut from 11 to 2,5 hrs.

On further increase of catalyst up to 3-5%, the yield of ester after vacuum distillation (the 180-185° fraction at 2 mm Hg) was 87-91% of theory.

The ester obtained had b.p. 230-235°/2 mm Hg; density,  $\rho_4^{20}$ , 0,9524; refractive index,  $n_D^{20}$ , 1,4535; acid number 0; ester number, 328; solidification point, below -70°C; and kinematic viscosity,  $\nu_{100}$ , 3,85 cc,  $\nu_{50}$ , 11,98 cc and  $\nu_{40}$  3769 cc.

It was shown that, in the presence of NaHSO<sub>4</sub>, the reaction temperature does not affect the duration of the process. Thus, the duration of esterification of trimethylolpropane with iso- and n-valeric acids in the presence of 7% of this catalyst remained equal to 2 hrs over the temperature range 110-160°C (Table 3).

It is known that in the presence of such catalysts as zinc oxide, aluminum oxide or also mineral acids, raising

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