Preparation of acetyl triethyl citrate by acetylation of triethyl citrate with acetic anhydride over a HZSM-5 zeolite catalyst

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Polyvinyl chloride (PVC) is among the most economically important polymers. It is widely used both in the form of rigid PVC and in the form of flexible PVC. To produce a flexible PVC, plasticizers are added to the PVC. In the majority of instances phthalic esters are used, particularly di-2-ethylhexyl phthalate, diisononyl phthalate and diisodecyl phthalate. However, it has been known that the phthalic esters represent a reproductive toxicity effects have in some instances already led to an increased level of identification marking under hazardous materials legislation. Therefore, the phthalate plasticizers are limited on the use in toys for toddlers, and it has to be assumed that the use of these phthalates will reduce markedly in the future, particularly in sensitive applications, such as food-or-drink packaging and medical applications. Therefore, there is a need for plasticizers which can be used for replacement of phthalates.

Acetyltriethylcitrate (ATEC) is an ester derived from citric acid, which can be used to replace phthalate esters as a green and nontoxic plasticizer in many plastic products such as toys, child care articles, food packages, medicinal instruments and so on. To date, this environmentally friendly plasticizer is mainly prepared by two methods, namely, the direct esterification of triethyl citrate (TEC) with acetic acid [1] and the acetylation of TEC with acetic anhydride [2].

The present study relates to TEC having an optionally acetylated, preferably acetylated, OH group, a process for the preparation of the TECs and the use of the TEC as plasticizers.

We present a preparation method of ATEC by acetylation of pentylcitrate with acetic anhydride on various acid catalysts. TEC was also prepared from citric acid monohydrate and ethanol to use as a raw material in the acetylation for the ATEC preparation. A methanesulphonic acid was employed as a homogeneous catalyst. HZSM-5 zeolites were also introduced as a heterogeneous catalyst in the reaction. Catalytic activities of the acid catalysts were evaluated in comparison with yields of ATEC.

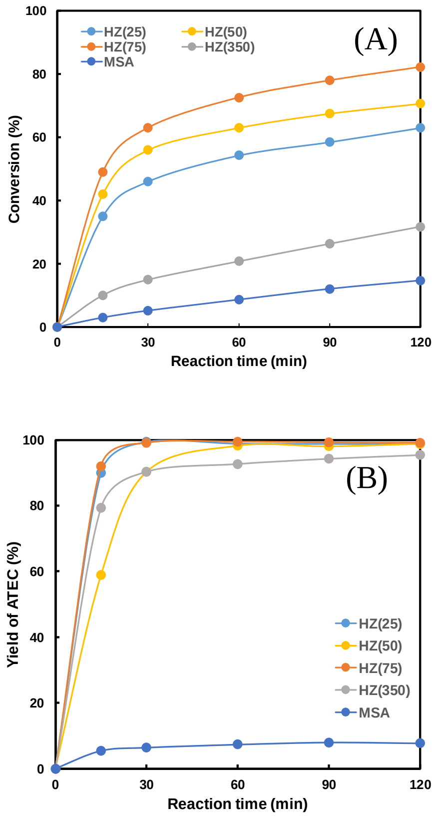

Fig. 1. Conversion of TEC (A) and yield of ATEC (B) on ZSM-5 zeolites.

Conversion of TEC and yield of ATEC shows in Fig. 1. The high conversion was obtained ca. 80% on HZ(75) zeolite. The yield of ATEC reached to ca. 96% on the zeolite catalyst. The mild acid strength of HZSM-5 zeolites led to high catalytic activity.

REFERENCES

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