"Green" synthesis of biolubricants catalyzed by ion-exchange resins

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Introduction

Due to its useful physical properties, biodegradable trimethylol propane trioleate (TMPTO) can be used in the production of hydraulic fluids. Currently TMPTO is being synthesized by esterification of fatty acids over homogeneous catalysts (e.g., p-toluenesulfonic acid). Although in view of the ecological and economic impact in the production of TMPTO, the importance of the application of heterogeneous catalysts is increasing drastically.

In this regards commercial ion-exchange resins possess high benefits for the environment. Families of Dowex and Amberlyst resins are highly acidic, stable chemically and mechanically [1].

This work compares two types of acidic ion-exchange resins with different degrees of cross-linking (divinylbenzene content) in the solvent-free synthesis of TMPTO.

Materials and Methods

Gel-type (Dowex-50WX2, with 4.8 eq/kg H^+ capacity) and macroreticular type (Amberlyst-36, with 5.4 eq/kg H^+ capacity) resins were studied in the reaction of esterification of oleic acid (OA) with thrimethylolpropane (TMP). Prior the catalytic test the "swelling" treatment was applied: the resins were heated at 120°C with TMP in the reactor for 1h30 under agitation. Then OA was added into the reactor and the catalytic test was started. The evolution of products within 24h was followed by the GC after adequate derivatization .

Results and Discussion

From the literature it is known that Amberlyst-36 possesses 12% of crosslinking compared to the Dowex-50WX2 (2%) [2]. The catalytic activity in the synthesis of TMPTO correlates with their crosslinking degree: the higher the crosslinking the lower the ability of the resin to swell. Thanks to better ability of swelling, Dowex provides higher accessibility of the active centers and thus higher activity (Figure 1A).

To confirm the necessity of the "swelling", the catalytic tests were run without the "swelling" step (e.g. resins were directly added to the mixture of TMP and OA, and the catalytic test was started immediately). Figure 1B demonstrates that Dowex loses drastically the activity without the "swelling" treatment. Contrary, for the Amberlyst the significance of the "swelling" step is less important due to the lower ability to swell.

Several recyclability tests (Figure 1C,D) show that after the 1st use, activity of the resins slightly diminishes in the reaction but remains stable in the further uses. An hypothesis is that during the first use some catalytic centers became poisoned by co-produced water. It is indeed known that water competes with the reactants for the active centers and is strongly bonded to sulfonic acid groups [1]. In the further uses there is equilibrium between "free" catalytic centers and the ones occupied by water as the latter was eliminated from the system by evaporation (the reactions were run in the open reactor).

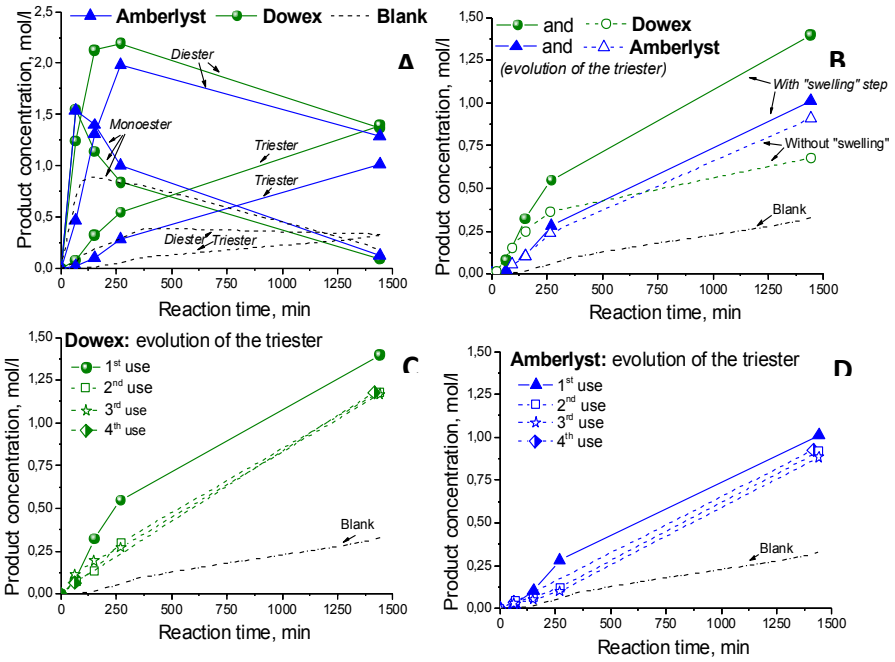

Figure 1. Catalytic performances of Dowex and Amberlyst in the solvent-free esterification of OA and TMP. A - evolution of mono-, di- and triesters (comparison of Dowex and Amberlyst); B-significance of "swelling" step (shown for the evolution of the triester); C-recyclability tests for Dowex; D-recyclability tests for Amberlyst (shown for the triester). Reaction conditions - 3:1 molar ratio of OA:TMP, 1.6% (wt.) of catalyst, no solvent, open reactor, 120°C, 400 rpm magnetic stirring.

Significance

Both investigated ion exchange resins are highly active and stable in the solvent-free synthesis of biolubricant. Due to the higher swelling ability (and hence, the better accessibility to active species), Dowex-50WX2 catalyzes the reaction more efficiently than Amberlyst-36. The activity of both resins remains stable within several re-uses. The current study shows high potential of the resins in the industrial application.

References

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