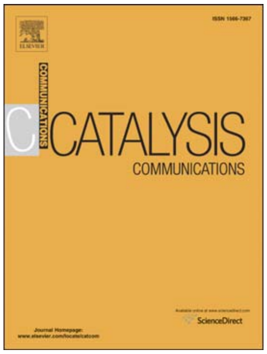

# Complementarity of Heterogeneous and Homogeneous Catalysis for Oleic Acid Esterification with Trimethylolpropane Over Ion-Exchange Resins

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# Complementarity of Heterogeneous and Homogeneous Catalysis for Oleic Acid Esterification with Trimethylolpropane Over Ion-Exchange Resins

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**Abstract** This work investigates the effect of Amberlyst 36, Purolite CT482 and Purolite CT275DR on the esterification of oleic acid with trimethylolpropane for production of the triester. The results assess that, while the three resins catalyze heterogeneously the formation of mono- and diesters, the final triester is generated thanks to the acidity of residual oleic acid. This cooperative scenario between heterogeneous and homogeneous catalysis is of first importance, as to complete the reaction over conventional heterogeneous catalyst was not feasible because of the strong steric hindrance of the intermediate product (diester) and the final product (triester).

**Introduction** Esterification of oleic acid (OA) with trimethylolpropane (TMP) is used in the industry for the production of a biolubricant, namely trimethylolpropane trioleate (TMPTO) [1]. TMPTO possesses useful physical properties such as high lubricity and viscosity indexes, high thermal stability, biodegradability, and so forth [2]. To our knowledge only homogeneous catalysts are being used to synthesize TMPTO at the industrial scale (e.g. p-toluenesulfonic acid, tin oxalate). As many homogeneous catalytic processes, the latter reaction requires additional separation, neutralization and purification steps. To minimize the separation procedure, in the industrial scale the reaction is being performed without additional solvent through stoichiometric conditions. Additionally, the replacement of homogeneous catalyst by heterogeneous one could bring even more benefits in the practical, economic and ecological aspects. This is the reason why extensive research is dedicated toward the finding of efficient heterogeneous catalyst which could be used in the industry [3-6].

To our knowledge, the available studies related to esterification of OA with TMP over heterogeneous catalysts are focused mainly on the comparative investigation of the catalyst activity and selectivity [1, 3, 6, 7]. Even though these reports often claim that the catalysts have high selectivity towards triester (50-90%), evaluation of real possibilities to use heterogeneous catalysts in industrial conditions for the synthesis of TMPTO is missing. As the presence of free fatty acids and mono- and/or diesters negatively affect the properties of final lubricant, the industrial application of these catalysts is valid only if the reaction is complete, with nearly 100% of OA conversion (selectivity towards triester being minimum 98% ) [2]. That is also why the esterification of OA with TMP should be performed with the stoichiometric ratio of reagents to avoid additional separation of OA.

Here we examine for the first time the possibility of acidic macroporous ion-exchanged resins to complete the tri-esterification of OA with TMP which is challenged by the industrial needs (the possibility to reach > 98% of triester selectivity).

## Materials and methods

*Chemicals.* Amberlyst 36 (mesh 600-850 µm) (Sigma), Purolite CT482 (425-1200 µm) and Purolite CT275DR (650 - 900 µm) was kindly provided by *Purolite* company , oleic acid 90% (Alfa Aesar), trimethylolpropane 98% (Alfa Aesar), pentadecane 99% (Sigma), N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) (Alfa Aesar). Acetonitrile, hexane and dimethylformamide (DMF) were of HPLC grade.

*Leaching test in DMF (elemental analysis).* 0,20 g of resin was placed into 10 ml of DMF and refluxed at 120°C for 19h. The amount of leached sulfur was measured in the filtered solution by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP AES).

*Esterification of OA with TMP.* 5.4 g OA and 0.86 g TMP (molar ratio 3:1) were placed into the batch reactor. The mixture was heated for 1 min to melt TMP, after which the catalyst (1.6% wt.) was added. The start of the reaction was considered after all components were mixed and the reactor was placed in an oil bath at 120°C (unless specified otherwise). The reaction was performed under magnetic agitation at 400 rpm and in an open reactor (unless specified otherwise). For sampling, 10 µl of the reaction mixture was taken at certain time intervals, derivatized as described below and followed by gas chromatography (GC). The separation on the GC system was performed with the method described in [8]. For the quantification, internal standard (pentadecane) was used (was added in the beginning of the esterification). In the chromatogram the evolution of mono-, di- and triesters was followed.

*Control tests.* Test with $H_2SO_4$ was performed under the same conditions as described above for the esterification. A "blank" test was performed under identical conditions but without the catalyst.

*Derivatization of esterification products.* Esterification products were derivatized with BSTFA following the protocol [8] with some modifications. 10 µl of the mixture was solubilized with 2 ml of acetonitrile. Then 500 µl of BSTFA was added and the final mixture was heated at 60°C for with vigorous agitation in a closed vessel. In 30 min the final products were extracted with 2 ml of hexane. The hexane extract was analyzed by GC. Standard deviations of the GC measurements were in the range of 0.04-0.20 (mol/l) for the detection of monoester, 0.03-0.15 for diester and 0.01-0.11 for the detection of triester.

*Conversion of OA.* The conversion of OA was calculated from the titration of the reaction medium at certain time intervals with solution of 0.1N KOH, according to the equation: *Conversion, % = (Initial amount of OA - Final amount of OA)×100/Initial amount of OA.*

## Results and discussions

Three resins were studied in this work: Amberlyst 36 (Amb), Purolite CT482 (Pur482) and Purolite CT275DR (Pur275). Their physico-chemical properties are summarized in table 1. All the studied resins belong to the macroporous family of acidic ion-exchange resins with comparable ion-exchange capacities. The main differences between these resins are their thermal stability and textural properties (case of Pur275).

**Table 1.** Properties of the studied resins

| Resin | Type | Max. operating temperature, °C | Sulfonation type[c] [9, 10] | Median pore diameter (dry resin), nm | Ion-exchange capacity, meq $H^+$/g | Leaching in DMF[b], mol % of sulfur (relatively to the initial amount of S) |
|---|---|---|---|---|---|---|
| **Amb** | Macro-reticular | 150 [11] | O | 27 [9] | 5.4 | 1.2 |
| **Pur482** | Macro-reticular | 190[a] | C | 26.8 [10] | 4.3 | 0.5 |
| **Pur275** | Macro-reticular | 180[a] | O | 40-70[a] | 5.2 | 3.3 |

[a] Provided by the supplier;

[b] ICP data (see materials and methods)

[c] Conventionally sulfonated (C), oversulfonated (O)

The catalytic test of OA esterification with TMP with Amb (Fig. 1) demonstrated that Amb accelerates the production of esters compared to the reaction without any catalyst ("blank-1" test). However, if compared to the homogeneous test over $H_2SO_4$, the concentration of the triester after 1500 min is 8 times lower when catalyzed by Amb in the identical conditions (the evolution of esters under $H_2SO_4$ is shown in the supplementary information, Fig.S1).

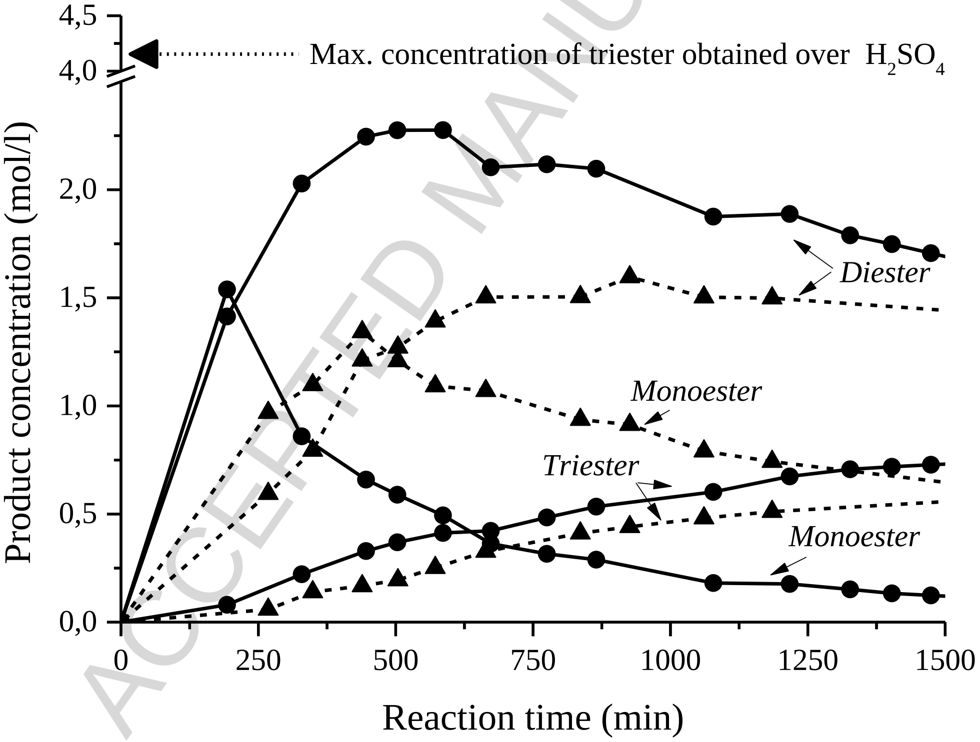

**Figure 1.** Evolution of mono-, di- and triesters concentration in the esterification of OA with TMP: ● - over Amb (test A), ▲ - "Blank-1" test. Reaction conditions: 3:1 molar ratio of OA:TMP, 1.6% wt. of catalyst, 120°C, 400 rpm, open batch reactor. The test with homogeneous $H_2SO_4$ is performed in the same conditions (evolution of the esters with time is shown in the supplementary information). "Blank-1" test is performed under the same conditions but without catalyst.

The conversion of OA over Amb reaches around 65% after 1500 min of the reaction (Fig. S2) whereas the obtained conversion of OA under identical conditions is nearly 100% over $H_2SO_4$ after the same time. Despite its lower productivity, industrial application of Amb for the production of biolubricant could be worthy if the final cost of the heterogeneous process is lower than of the homogeneous one. An indispensable requisite for this is that triester remains the main and ideally only product of the reaction.

In this work we thus examine the possibility of ion-exchange resins to complete the tri-esterification of OA with TMP under conditions close to the industrial ones (stoichiometric amounts of reagents and continuous removal of water to shift the equilibrium towards the products). For this purpose we run the reaction with Amb for 450 min after which we removed the Amb and continued following the evolution of esters with time. The latter test was compared to the reaction where Amb was present continuously (Fig. 2). The kinetic curves of the formation of esters after the catalyst was removed (test B) superpose with the curves where the catalyst was present continuously (test A). This scenario indicates that the catalyst either lost its activity or was leached in the liquid reaction medium. However, ICP analysis of the dimethylformamide medium (DMF) after interacting with Amb (leaching test) revealed the presence of only 1.2 mol% of S-species relatively to the total amount of S within the resin (Table 1).

To address the possibility of deactivation caused by water that may block the active centers of the resin, we added fresh Amb to the reaction mixture after 1350 min from the start of the test (Fig. 2; test B, where the catalyst was removed previously). The results show that even after insertion of the fresh catalyst the activity does not change compared to the test A. Shortly speaking, after several hours of the reaction the ester production does not depend on the presence or absence of the heterogeneous catalyst. This observation means that the lack of activity after several hours of catalytic test is not due to the poisoning of active centers.

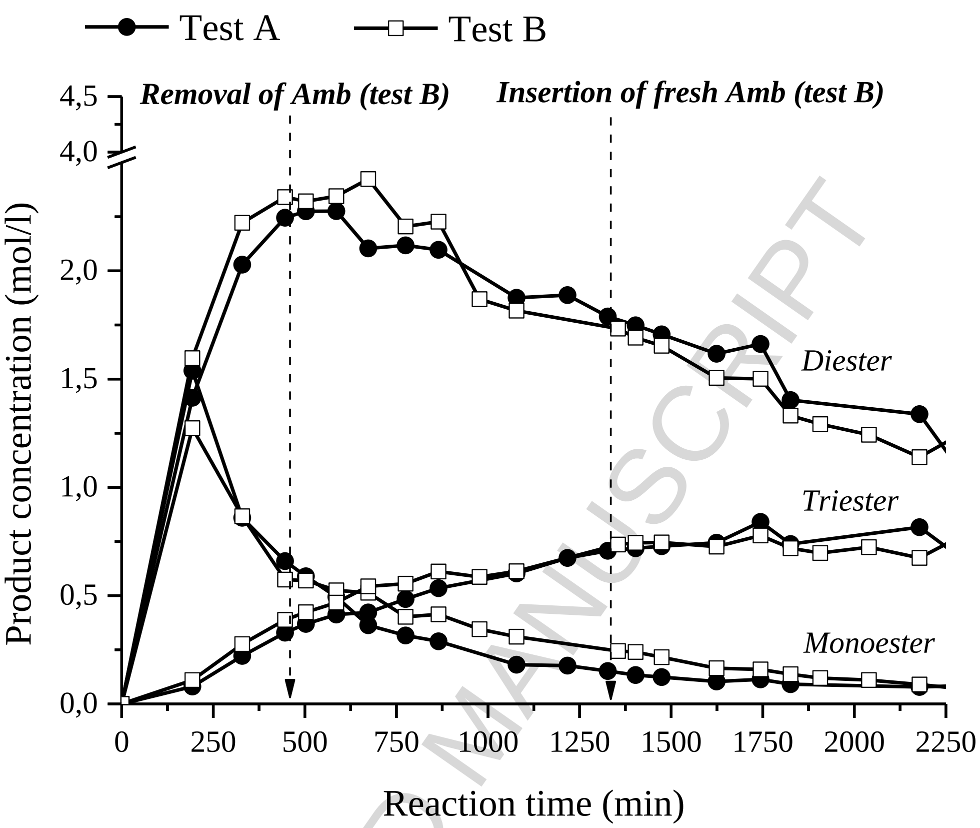

**Figure 2.** Evolution of mono-, di- and triesters concentration in the esterification of OA with TMP: ●— Presence of Amb continuously (test A), □— Removal of Amb after 450 minutes from the beginning of the reaction and new insertion of fresh Amb after 1320 minutes (test B). Reaction conditions: 3:1 molar ratio of OA:TMP, 1.6% wt. of catalyst, 120°C, 400 rpm, open batch reactor.

To explore the behavior of the system at higher temperature we performed some tests with Purolite CT482 (Pur482) and Purolite CT275DR (Pur275) bearing higher thermal stability than Amb. Moreover, Pur275 has bigger permanent pores that could be beneficial in the intraparticle mass transfer. For the test with Purolites (at 180°C) we first started the reaction without catalyst to be able distinguishing the “pure” heterogeneous catalysis from homogeneous one. Esterification is indeed homogeneously catalyzing thanks to free OA. After the concentration of OA decreased (to 15% from initial amount) we added resin and continued following the OA conversion. Figure 3a shows the curves of OA conversion as a function of time for the “Blank-2” test and the test with Pur482. We notice that the curves for both tests superimpose, showing that at 180° the presence of Pur482 does not accelerate the OA conversion. Interestingly, although Pur275 has higher number of active sites and bigger pores compared to Pur482 (Table 1), the behavior of Pur275 at the end of the reaction does not differ from the Pur482 (Fig. 3b). The latter suggests that the inefficiency of the resins at the end of the reaction does not come from the internal diffusion limitations caused by small pores. Moreover, it is clear that both Purolites do not catalyze the end of the reaction and that it is high temperature instead that helps to accelerate the third esterification.

We should mention that when used in the beginning of the reaction, both Pur482 and Pur275 accelerate the formation of the esters as Amb did as well (the evolution of esters with time is shown in Fig. S3). Pur275 showed to be more active in this case compared to Pur482 and Amb.

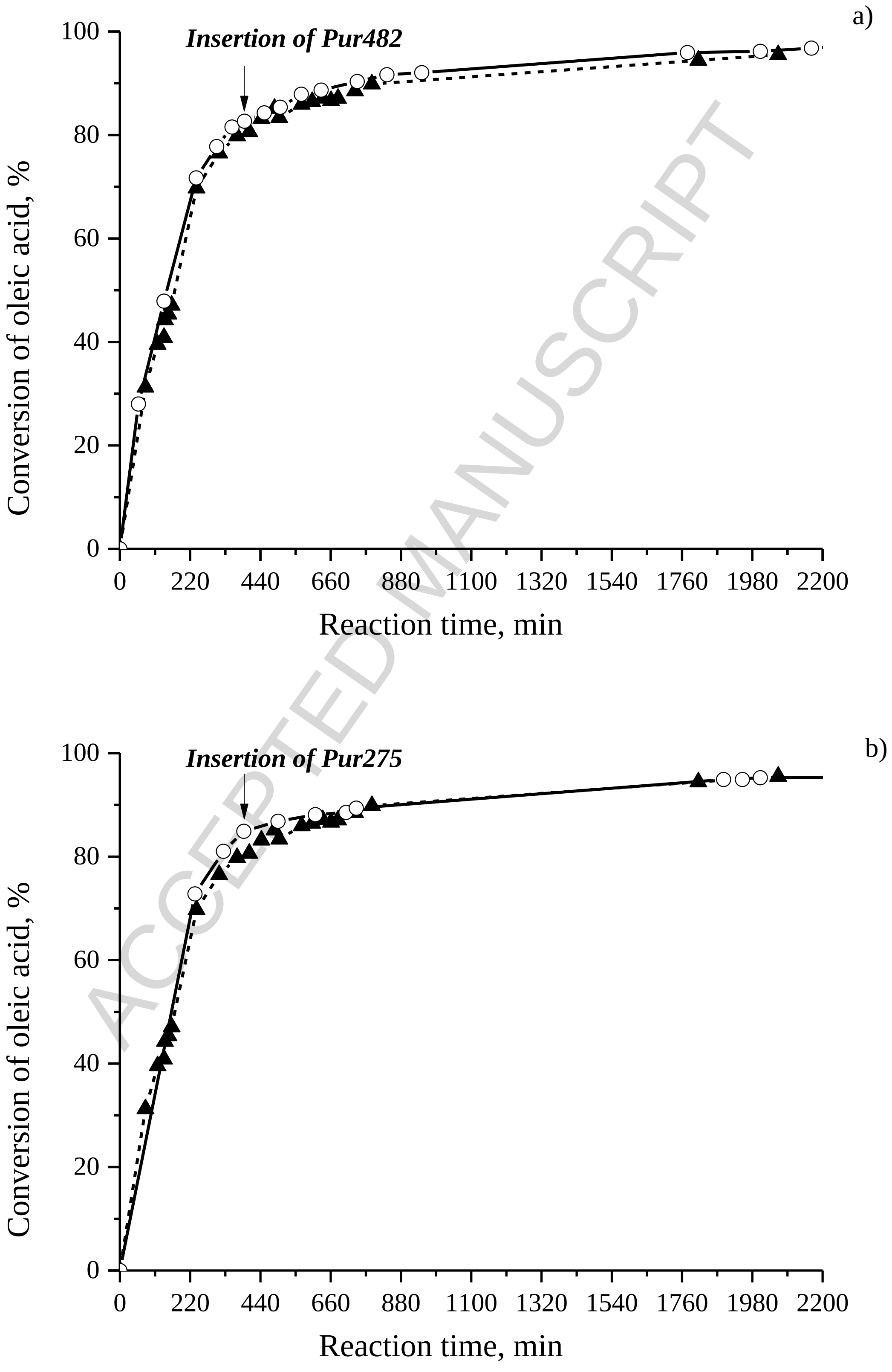

**Figure 3.** Conversion of OA with TMP. Reaction conditions: 3:1 molar ratio of OA:TMP, 1.6 %wt. of catalyst (except "blank" test), 180°C, 400 rpm, continuous flow of $N_2$ (closed batch reactor connected to distillation

apparatus) .a) ▲"Blank-2" test (no catalyst, the same conditions); ○ Reaction started as "blank" (no catalyst), then after 340 min Pur482 was added; b) ▲"Blank-2"; ○ Reaction started as "blank-2" (then after 340 min Pur275 was added).

Thus, neither Amb at 120°C nor Purolites at higher temperature are able to complete the tri-esterification whereas they are able to convert OA to monoester and monoester to diester. Likely because of steric hindrance of these intermediate products the last step of the process - conversion of the diester to the triester - is not possible over conventional heterogeneous catalyst. The results also indicate that the formation of the triester is occurring due to the acidity of the residual OA. When OA is being consumed and its concentration decreases, the production of the triester is no longer persistent regarding the low concentration of homogeneous OA. Heterogeneous catalyst in this case becomes inefficient due to the difficulties in adsorption/desorption and diffusion processes of bulky components (di- and triesters) on its surface and/or in its structure.

## Conclusions

Amberlyst 36, Purolite CT482 and Purolite CT275DR were studied in the industrial process for the tri-esterification of OA with TMP. Our studies showed that Amb, Pur482 and Pur275 catalyze only the conversion of OA to monoester and of monoester to diester and do not catalyze the conversion of diester to triester. The reason for latter is steric hindrance of the di- and tri-esters that complicates their adsorption/desorption and diffusion on the catalyst surface and in its structure. On the one hand, these penalties make impossible to complete the esterification of OA with TMP over heterogeneous catalyst. On the other hand we showed that final diester to triester conversion is induced exclusively through homogeneous catalysis. This complementarity between homogeneous and heterogeneous catalysis is of primary importance as it contributes first toward the understanding of complex sequential catalytic reactions. Secondly, it provides key information for the design of advanced heterogeneous catalysts capable, for instance, bearing endeavor for partial solubilization/reprecipitation where homogeneous catalysis would proceed.

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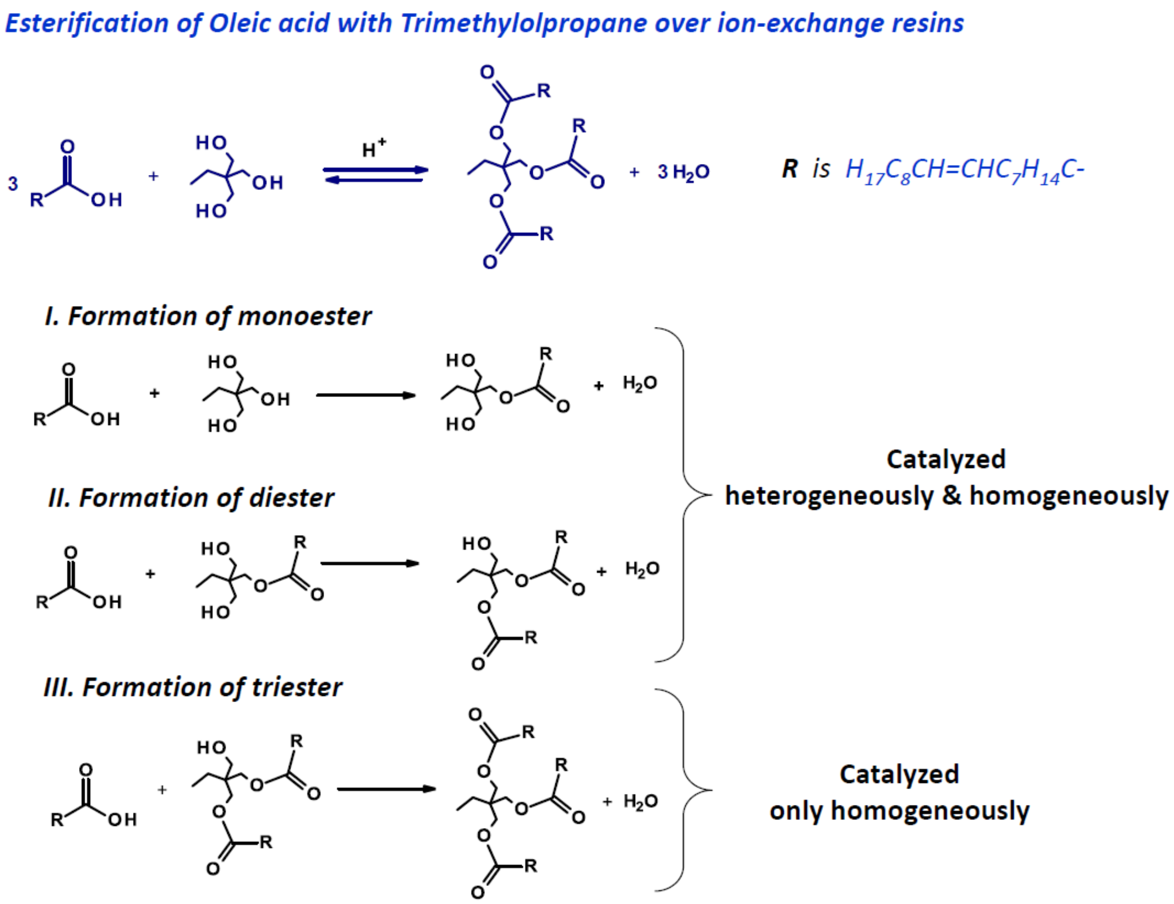

Graphical abstract

## Highlights

Ion-exchange resins were studied in the tri-esterification of OA with TMP.

The final triester is homogeneously generated thanks to the residual oleic acid.

Bulky di- and triesters hinder adsorption/desorption onto resin surface.