Improving the Catalytic Performance of Ion Exchange Resins in the Etherification of Glycerol with Isobutene

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Ion exchange resins are successfully used as catalysts to convert bio-derived glycerol into its tert-butyl ethers by reaction with isobutene. Here we employ emulsifiers in order to increase the overall process performance as measured by glycerol conversion and selectivity of isobutene to ethers. We have tested the influence of two cationic surfactants on the glycerol conversion and on the distribution of reaction products and observed that use of the appropriate emulsifying agent increased the glycerol conversion favoring the formation of ethers. Moreover, we have systematically investigated the influence of isobutene to glycerol molar ratio and of initial pH of the reaction environment on the performances of the etherification process. Based on the results observed we propose that emulsifiers improve the access of isobutene to the catalyst surface, thus promoting the formation of reaction intermediates in the glycerol phase. However, when the concentration of isobutene is greater than the optimum value the undesired isobutene oligomerization reaction becomes important and the overall process performance declines.

Keywords: glycerol, etherification, isobutene, Purolite CT 275, catalysis, emulsifiers, multiphase

Glycerol is the main by-product in the transesterification reaction of vegetable oils (i.e. rapeseed or soybean oil) with methanol. Its production is equivalent to approximately 10 %(wt.) of the total biodiesel produced [1-2] According to the European Biodiesel Board, the production of biodiesel in the European Union (EU) peaked at 9.6 millions of metric tons (MTm) in 2010, with a fast annual increase of about 25% from year 2000 [3-4]. The European Council of March 2007 and Renewable Energy Directive (RED) 2009/28/EC of the EU have stated that member states should ensure a proportion of 10% of biofuel in transport petrol and diesel consumption by the year 2020 [5]. Even if overall biodiesel production in EU countries showed stagnation in 2011, a corresponding glycerol production of about 1 MTm per year in EU can be estimated for the current period as well as forecast for the whole decade [3] .

Consequently, miscellaneous research strategies are pursued in order to find new applications for the constantly growing availability of glycerol as a low-cost feedstock. These strategies include selective oxidation, hydrogenolysis to propylene glycol, dehydration to acrolein, fermentation towards 1, 3-propanediol, synthesis of epichlorohydrin, or even reforming towards syngas [2, 6]. In addition to these alternatives, transformation of glycerol into fuel oxygenates by means of etherification [7] and esterification [1] reactions is also being explored. A special interest was given to the preparation of alkyl ethers of glycerol by etherification with isobutene [7] .

In presence of acid catalysts, isobutene reacts with glycerol to yield a mixture of mono-, di-, and tri-tert-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively). The higher ethers (DTBG and TTBG) are excellent additives with large potential for diesel and biodiesel formulations. These oxygenated compounds, when incorporated into standard diesel fuels, have led to a decrease in particles, unburned hydrocarbons, carbon monoxide and aldehydes emissions [8]. Likewise, ethers can act as cold flow improvers for diesel fuel, reducing its viscosity [7]. This may be a significant breakthrough due to the growing demand of new additives, specifically for biodiesel, that are biodegradable, non-toxic and renewable. In addition, such derivates can also be used as octane boosters for gasoline, as an alternative to commercial trialkyl ethers (MTBE and ETBE) [8] .

Klepacova et al. [8] studied the etherification of glycerol by isobutene or by tert-butyl alcohol over commercial, strong acid ion-exchange resins Amberlysts (A 15, 35, 36, 39, 119) and compared the etherification performance of these catalysts with the results obtained using large pore zeolite catalysts. These authors observed their best results with the dry form of the A35 catalyst (7.5 % wt.) at 60°C, an isobutene to glycerol molar ratio of 4:1, and reacting for 8 hours. Under these reaction conditions the total conversion of glycerol was reached, while the highest yield of di- and tri-ether obtained was 86.6% for A15 and 88.7% for A35. Zeolites, H - Y and H - Beta, provided lower selectivity than ion-exchange resins, while the tri tert-butyl ether of glycerol (TTBG) is not formed at all over H-Beta zeolite.

Karinen and Krause [1] also studied the effect of the reaction conditions on liquid phase glycerol etherification with isobutene, using the A35 acid ion exchange resin as catalyst. These authors observed that ether product distribution can be controlled by adjusting the reaction conditions. For example, they noticed that at 80°C both the reaction rate and the distribution of products depend on the stirring rate when this is in a range below 1300 rpm. In the experiments they carried out, the etherification was the primary reaction. However, isobutene oligomerization to C8, C12 and C16 hydrocarbons occurred simultaneously with the etherification reaction and is favored by the same acid function of the catalyst. Glycerol polymerization to polyglycerols did not take place on these acid catalysts in the temperature range used for isobutene etherification.

Interestingly, a complete conversion of isobutene could not be reached, even after a reaction time of 7 h, because

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when the complete conversion of glycerol had been achieved, 70-80% of isobutene was consumed and, after that, the isobutene consumption diminished drastically. Analyzing comparatively their results, Karinen and Krause [1] concluded that a higher selectivity in ethers is always coupled with the decrease in the amount of oligomers formed. The two authors consequently inferred that mass transfer issues are influential for the overall performance of the glycerol etherification process as expressed by the glycerol conversion and isobutene selectivity to ethers.

In the present contribution we report our results in the attempt to enhance the performance of macroporous ion exchange resin catalysts in the reaction of glycerol with isobutene by carrying out the reaction in the presence of emulsifiers, which, presumably forming an emulsion, improve the mass transfer between the two liquid phases – the glycerol polar phase and the isobutene nonpolar phase – in contact during the process.

Experimental part

The reagents used in the etherification tests were analytical grade purity glycerol from CHIMOPAR and 99 % (wt.) isobutene from Linde. Purolite CT 275, a strong acid, macroporous ion-exchange resin, containing 5.2 miliequivalent/g sulfonic active sites, served as catalyst for all the experiments. Prior to each experiment, 7.5 g catalyst were washed with methanol in order to remove water and other impurities, then dried and subsequently swollen in glycerol before being loaded into the reactor.

The etherification experiments were carried out in a stainless steel Berghoff autoclave of 700 mL volume. The reactor is placed in an electric heater equipped with a high-performance temperature controller and manometer. The stirring rate is accurately controlled up to 1500 rpm. For each test the batch reactor was first loaded with the swollen catalyst and the glycerol feed, then closed and purged with nitrogen. Subsequently, liquid isobutene was charged to reach the desired isobutene to glycerol molar ratio. After completing the loading procedure, the pressure in the reactor was 2.5 atm at room temperature. The reactor was then heated to 80°C in approximately 40 minutes. When the temperature stabilized the pressure in the reactor was approximately 12 atm – the vapor pressure of isobutene at 80°C – indicating the presence of *free* isobutene, liquid and vapor, phases. Then stirring was started and the stirrer controller was set at 1300 rotations per minute, stirring rate beyond which a further increase has no effect on the process performance, consistent with data reported by other authors [1] .

All batches were reacted for 5 h and the pressure in the autoclave was continuously monitored during the whole experiment. At the end of each experiment, when the pressure dropped to approximately 2 atm, the autoclave was left to cool down to room temperature, the eventual excess of unreacted isobutene was purged off and the autoclave depressurized. The reactor was weighted before and after loading the catalyst and the glycerol, after loading the isobutene, and after release of the unreacted isobutene, in order to obtain accurate data for the material balance. Reaction products were analyzed by gas-chromatography using a Network 5890 GC from Agilent Technologies, equipped with flame ionization detector and a polar column DB-WAX of 30 m length and 0.32 mm inner diameter, operated with a temperature program between 20 and 250°C. All the experiments were performed at 80°C using 113 g of glycerol at different isobutene to glycerol molar ratios and different values for the *p*H of the initial glycerol phase.

Because mass transfer between the two liquid phases is an important issue for the etherification reaction of glycerol with isobutene, as demonstrated by Karinen and Krause [1], we tested whether performing the reaction in the presence of an emulsifying agent will improve the performance of the catalyst. For these tests two cationic emulsifiers were added to the mixture of reactants at 0.1 % (wt.) concentration with respect to the whole amount of reactants. The emulsifying agents used were: (i) ROT 1, that is 2-alkyl-1-polyethylene-polyamine-imidazoline (7.52 % amino nitrogen content) from Atica Chemicals; (ii) AND, that is the diamide of 4 azasebacic acid with triethylene-tetraamine (12% amino nitrogen content), with the structures given in figure 1. Both surfactants have a hydro-phile - lypophile balance that facilitates the formation of direct emulsions. The two emulsifiers were prior conditioned by neutralization with phosphoric acid aqueous solution 85 % (vol.).

Results and discussions

In all glycerol etherification tests, independent of the reaction conditions used, the following products were obtained:

- two mono-ether isomers in proportions similar to those reported in the literature [8];
- two di-ether isomers, also obeying the ratio reported in the literature;
- the tri-ether;
- isobutene oligomers (mainly isooctenes), accounted for as unselective by-products.

All these products and their retention times were identified by comparison with chromatographic standards and/or by mass spectrometry (i.e. di-ethers and tri-ether).

Since the main objective of the present investigation was to improve the catalytic performance of the ion exchange resin Purolite CT275 in the glycerol etherification process, the results obtained will be further reported in a manner that allows a direct assessment of the effects of emulsifying agents in the reaction mixture. Figure 2 shows

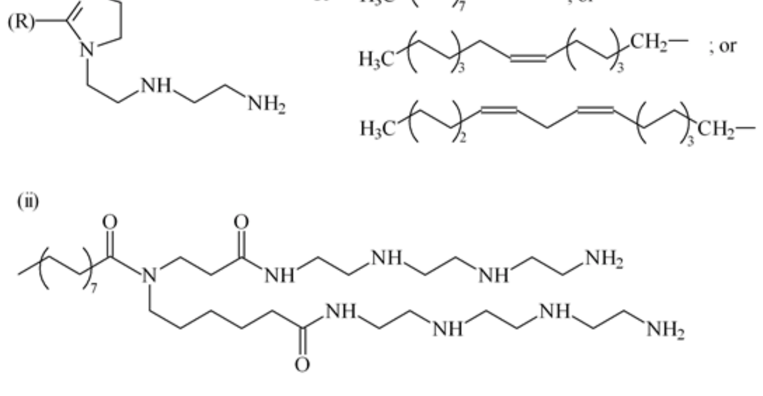

Fig. 1. Structures of emulsifiers: (i) ROT 1; (ii)AND

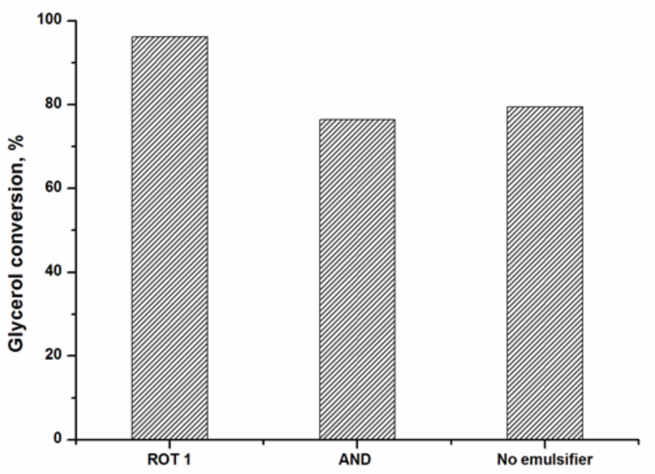

Fig. 2. Glycerol conversions obtained with and without emulsifying agents in the presence of Purolite CT275 catalyst at *p*H=1.5.

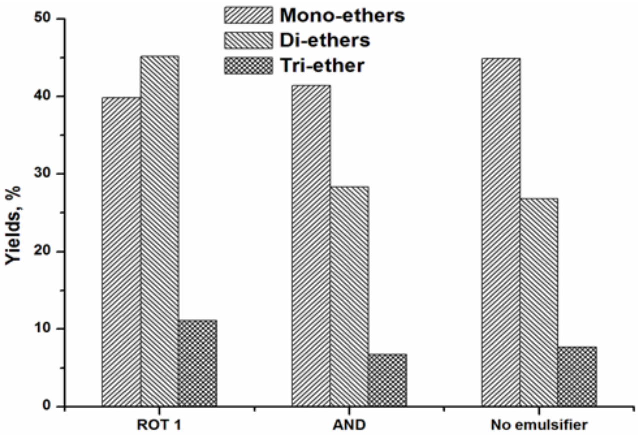

Fig. 3. Yields of the etherification products with and without emulsifiers at isobutene to glycerol molar ratio of 1.5 and *p*H=1.5.

the values of glycerol conversions obtained under identical reaction conditions (i.e. same amounts of catalyst and reactants, glycerol to isobutene molar ratio, temperature, stirring rate and duration of test), but with and without emulsifying agents.

When AND surfactant is added, the conversion of glycerol is similar to that obtained without emulsifier and reaches approximately 80 %, while ROT 1 emulsifier leads to a conversion value above 95 %. One may easily conclude that the presence of emulsifiers may improve the performance of the CT275 catalyst, but their effect definitely varies according their structure. However, an increase of 15% in conversion under identical reaction conditions indicates significant potential for improvement in the efficiency of an industrial process, therefore it cannot be neglected.

In order to complete the picture of the surfactants effect on the performance of the etherification process, the distributions of the etherification products determined in aforementioned tests are presented in figure 3 below. As expected, the tests performed without emulsifier or in the presence of AND, gave similar distribution of the ethers produced, as for glycerol conversion. However, in the presence of ROT 1 emulsifier the yields to superior ethers (i.e. di- and tri-ethers) are significantly higher – with approximately 20 and 5%, respectively – while the yield to mono-ether is lower by only 3 to 5%. These results show that the utilization of an appropriate emulsifier may considerably increase not only the glycerol conversion, but also the selectivity to heavier ethers.

It is worth noting that the 3% to 5% decrease in the yield of mono-ethers observed with ROT 1 is appreciably lower than the approximately 23% gain in the yield of superior ethers. The large differences between polarity and densities of two liquid phases cause low mutual solubility and rapid gravitational separation. In the operating conditions of our experiments, the solubility of glycerol in isobutene (less than 0.03 % wt.) is much lower than the solubility of isobutene in glycerol (about 15 % wt.). Moreover, because the catalyst is swollen in glycerol and has a significantly higher affinity for polar solvents, its grains are dispersed mainly in the glycerol phase and isobutene needs to dissolve into the glycerol phase in order to reach the catalyst surface. The results obtained with and without ROT 1 suggest that this emulsifier actually allows faster access of isobutene to the catalyst surface where the reaction occurs, so that the reaction intermediate species react further with a second, or even a third hydroxyl group before the reaction ceases, which eventually means better mass transfer of isobutene into the polar glycerol phase. Since the only difference between the two tests is the presence of ROT 1, the enhanced mass transfer may only arise from a larger mass transfer surface area between the two phases. At the same stirring rate, a larger surface area may result from the generation of smaller droplets of isobutene dispersed in the glycerol phase, or, in other words, from the formation of an isobutene emulsion in glycerol. If this is the case, then selectivity to isooctene oligomers should drop significantly as dimerization requires high local concentration of isobutene near the active sites of the catalyst. Indeed, the yield of isooctenes in the presence of ROT 1 is about half of that observed without emulsifier, as depicted in figure 4 below.

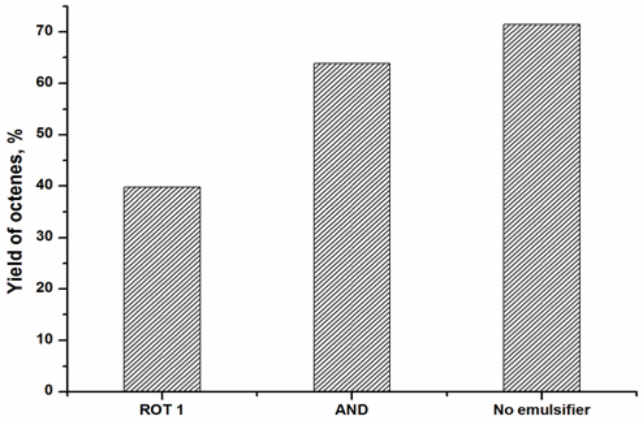

Fig. 4. Yields of isooctenes with and without emulsifiers at isobutene to glycerol molar ratio of 1.5 and *p*H=1.5

Interestingly, the second emulsifier used did not produce any significant improvement in the performance of the etherification process, suggesting the AND emulsifier does not succeed to produce an emulsion of isobutene in glycerol under the reaction conditions. However, one can note a small drop in the isooctenes yield, showing there is potential for improvement of the process performance with AND surfactant too, e. g. through a tighter correlation between reaction conditions and its emulsifying properties.

To check for the formation of emulsions between glycerol and isobutene in the presence of the two surfactants, we have carried out separate tests with equal amounts of glycerol and 1-hexene which have been mixed together at room temperature in a glass vessel in the presence of ROT 1 or AND. The glycerol – hexene mixture with ROT 1 readily formed an emulsion which was stable for several days after ceasing the stirring. However, in the presence of the AND emulsifier two liquid phases were separated within 15 s after the end of the mixing, proving

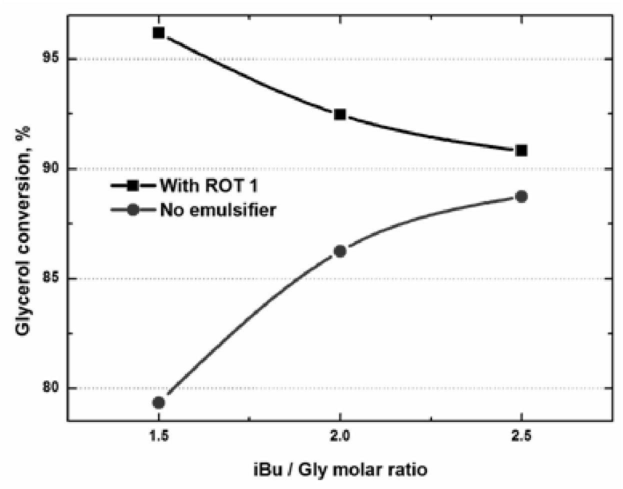

Fig. 5. Glycerol conversion at *p*H=1.5 for different isobutene to glycerol molar ratios in presence and in absence of ROT 1 emulsifier

that ROT 1 is a significantly more effective emulsifier for the glycerol - olefin system than AND.

We have further systematically investigated the effect of two process parameters – the isobutene to glycerol molar ratio and the *p*H of the glycerol phase – likely to influence the glycerol conversion and the isobutene selectivity to ethers. Figure 5 shows the variation of the glycerol conversion with the isobutene to glycerol molar ratio for the CT275 catalyst with added ROT 1 in comparison with the results obtained with the same catalyst, but without emulsifier. We mention that these results were obtained at *p*H = 1.5 for the glycerol phase, both with and without surfactant, the pH being adjusted by addition of phosphoric acid solution 85 % (vol.).

As already discussed, the glycerol conversion is significantly higher in the presence of ROT 1 emulsifier. Interestingly, in the presence of ROT 1, the glycerol conversion declines approximately 5 % as the isobutene to glycerol molar ratio is risen from 1.5 to 2.5, while without emulsifier the glycerol conversion grows by almost 10 %. We should recall that the amount of glycerol in the reactor was always the same, and the isobutene to glycerol molar ratio was adjusted by increasing the amount of isobutene added into the reactor.

This behavior suggests a competition between isobutene and glycerol molecules for the same active sites of the catalyst, with isobutene likely to win against the latter. Along these lines, in the presence of ROT 1, more isobutene dissolves into the glycerol phase, so that glycerol at catalyst surface is able to react with isobutene dissolved in the polar phase to produce mono-ethers. When the isobutene to glycerol ratio is grown, and as the concentration of ethers in the glycerol phase becomes higher, the concentration of isobutene molecules in the polar phase increases, so isobutene molecules start to react among themselves, thus competing with glycerol and mono- and di-ether molecules. Thus, the growth of the isobutene concentration in the polar phase is observed to lead to an increase in the conversion of isobutene to oligomers. This behavior suggests that glycerol, mono-ether and di-ether react with dissolved isobutene, while same dissolved isobutene when reaching the catalyst surface can concurrently undergo reaction with itself to form oligomers.

In contrast, in the absence of emulsifiers when the mixing between the two phases is less effective and the mass transfer surface area is reduced, the isobutene concentration in the glycerol phase is lower, thus allowing more glycerol to react with the isobutene dissolved in the polar phase to form mono- di- and tri-ethers. The higher glycerol conversion observed with the increase in the isobutene to glycerol molar ratio is most likely due to longer lasting of the free isobutene phase in the reactor, as confirmed by the evolution of pressure in the reactor recorded during each test. As the glycerol phase enriches in ethers, the solubility of isobutene and its concentration in the glycerol phase become greater allowing more ethers to form, hence increasing the glycerol conversion. However, simultaneous increase in the nonselective isobutene conversion is also expected since both ethers and oligomers actually form at the catalyst surface in the polar phase. This assumption is consistent with the variation of the isobutene conversion to ethers when the isobutene to glycerol molar ratio is increased from 1.5 to 2.5 as shown in figure 6 which illustrates different behaviour for the two cases, although both conversions change in the same direction.

As discussed above, conversion of isobutene to ethers is strongly dependent on the concentration of isobutene dissolved in the polar phase. The drop in the isobutene conversion to ethers associated with the increase in the isobutene to glycerol molar ratio is most likely due the increase of the isobutene concentration in the polar phase favoring the preferential reaction of isobutene to oligomers. In the presence of ROT 1, when the mass transfer between the glycerol and the isobutene phases is improved by increasing the contact surface area between the two phases, the drop in isobutene conversion to ethers is sharper due to the faster increase of the concentration of isobutene in the polar phase. However, in the absence of emulsifier, because the free isobutene phase likely lasts longer when the isobutene to glycerol ratio used was 2.5 compared to 1.5, the drop in isobutene conversion to ethers becomes comparable to that observed in the presence of ROT 1.

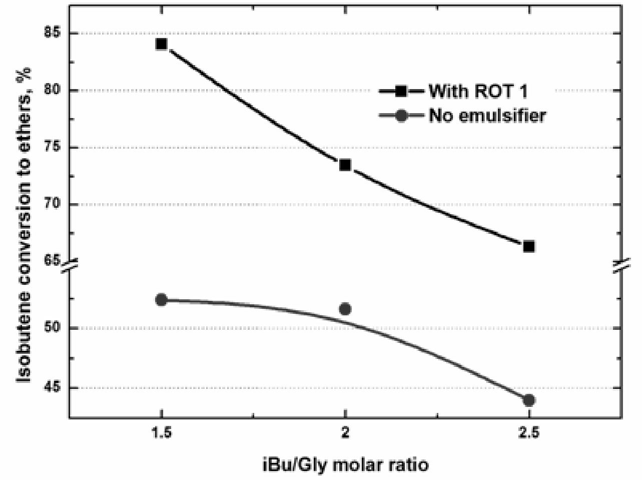

Fig. 6. Isobutene conversion to ethers at *p*H=1.5 for different isobutene to glycerol molar ratios in presence and in absence of ROT 1 emulsifier

If our assumption is correct, there must be significant differences in the distribution of the ethers produced in the presence and in the absence of ROT 1. The yields of mono- di- and tri-ether observed under identical operating conditions, with the presence of the emulsifier as the sole difference, are shown in figur e7 for three isobutene to glycerol ratios.

The results of figure 7 suggest that, at isobutene to glycerol molar ratio of 1.5, the concentration of isobutene in the polar phase is lower in the absence of ROT 1, consistent with the lower glycerol conversion; thus, the glycerol molecules remain at the catalyst surface for longer time and react with full conversion of hydroxyl groups to

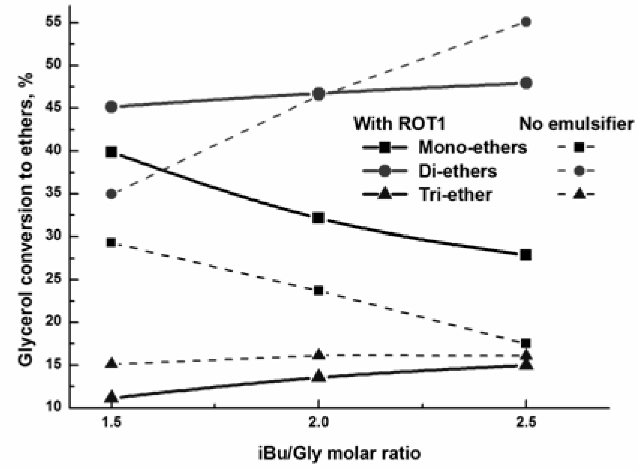

Fig. 7. Variation of the yields of ethers at *p*H=1.5 with the isobutene to glycerol molar ratio, with or without ROT 1 emulsifier.

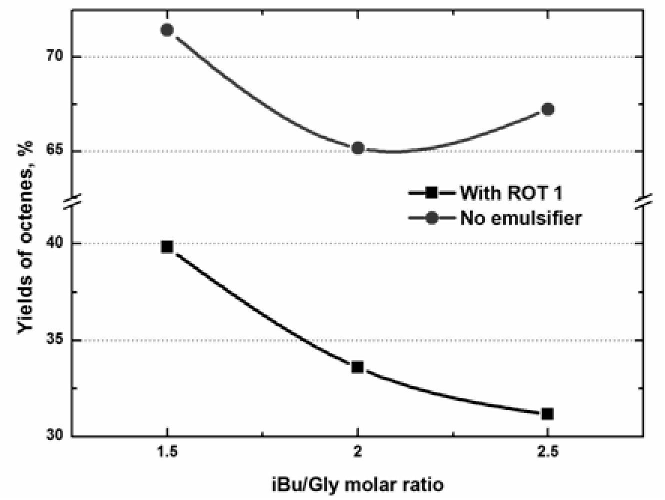

Fig. 8. Yields of isooctenes resulted at *p*H=1.5 for different isobutene to glycerol molar ratios in presence and in absence of ROT 1 emulsifier.

tri-ether. In presence of ROT 1, the concentration of dissolved isobutene is higher forming more ethers and resulting in higher glycerol conversion. With the rise of isobutene to glycerol molar ratio to 2, in the absence of emulsifier, the increase in the isobutene concentration is only due to the ethers concentration enhancement in the glycerol phase, and because the free isobutene phase lasts longer in the reactor, the glycerol conversion increases, but primarily due to the higher conversion to mono-ethers and di-ethers. It should be noted here that this increase in glycerol conversion is almost quantitatively reflected in the increase of isobutene total conversion to ethers (fig. 6), suggesting that isobutene is more selectively converted into ethers under these conditions than at molar ratio of 1.5. However, the further growth of the glycerol conversion associated with the increase in the isobutene to glycerol molar ratio to 2.5 in the absence of ROT 1 is actually accompanied by a pronounced intensification of the oligomerization reaction, yet the selectivity to higher ethers increases faster than in the presence of emulsifier. It is worth noting that the yield in tri-ether obtained in the presence of ROT 1 is still lower than that observed in the absence of emulsifier (fig. 7), which suggest that in the absence of ROT 1 most of the tri-ether is formed at low glycerol conversion, while with emulsifier the tri-ether forms at higher glycerol conversions. Such behavior would imply a negative overall reaction order with respect to isobutene for the formation of tri-ether from di-ether, or a reversible and equilibrated conversion of di ethers to tri-ether. The enhancement of the isobutene concentration in the polar phase can induce a significant increase of the oligomerization rate and a decrease in the conversion of di-ethers to tri-ether, consistent with an apparent negative reaction order with respect to isobutene in the etherification of di-ethers.

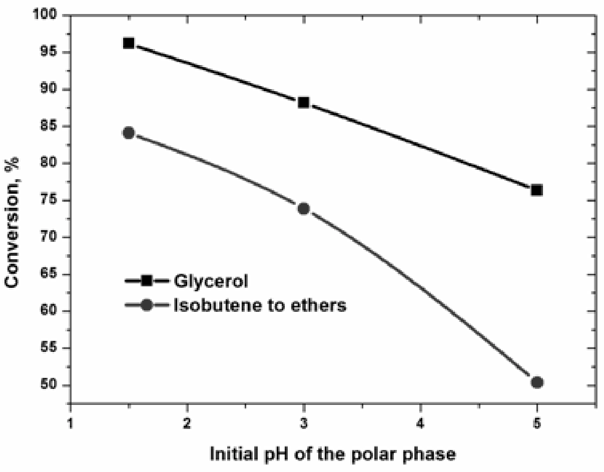

Fig. 9. Glycerol and isobutene conversions to ethers with the isobutene to glycerol molar ratio of 1.5 for different initial *p*H values of the polar phase in presence of ROT 1

These interpretations are also consistent with the variation of the isooctenes yield with the isobutene to glycerol molar ratios depicted in figure 8. Indeed, in the absence of ROT 1 the initial increase in the isobutene to glycerol molar ratio to 2 causes a decrease of the yield in oligomers, while a further growth to 2.5 leads to the increase of the same yield, in agreement with a faster increase of the oligomerization reaction rate rapidly depleting the isobutene dissolved in the polar phase.

When the initial *p*H of the glycerol phase was varied by adding different amounts of phosphoric acid solution, the glycerol and the isobutene conversions to ethers, obtained at 80°C in presence of 0.3 g of ROT 1 with an isobutene to glycerol molar ratio of 1.5, changed as shown in figur e 9.

Studying the influence of the *p*H of the reaction environment on the performance of the etherification process revealed higher conversions at lower *p*H, suggesting the concentration of isobutene in the polar phase is higher as the acidity of the reaction environment increases. Since the emulsifying efficiency of cationic emulsifiers usually increases with their degree of ionization, one may speculate faster mass transfer of isobutene into the polar phase at lower *p*H. If this was the case we should also expect higher yields in isobutene oligomers as the initial *p*H of the polar phase is lower. To our surprise, as the initial *p*H of the polar phase is more acidic the yield in isooctenes is lower, although both glycerol and isobutene conversion values are the highest, as depicted in figure10 below.

This behavior suggests the emulsifier, which has a base character, adsorbs strongly on the acid sites of the catalyst, inhibiting their catalytic activity both for etherification and oligomerization reactions. The higher is the initial *p*H of the polar phase, the fewer are the acid sites available for reaction and the competition is won by the isobutene molecules resulting in higher yields of oligomers. As more phosphoric acid is added initially to the glycerol phase, fewer acid sites are blocked by emulsifier molecules and become available for reaction, thus increasing both glycerol and isobutene conversions, simultaneously improving the mass transfer and, thus, the isobutene concentration in

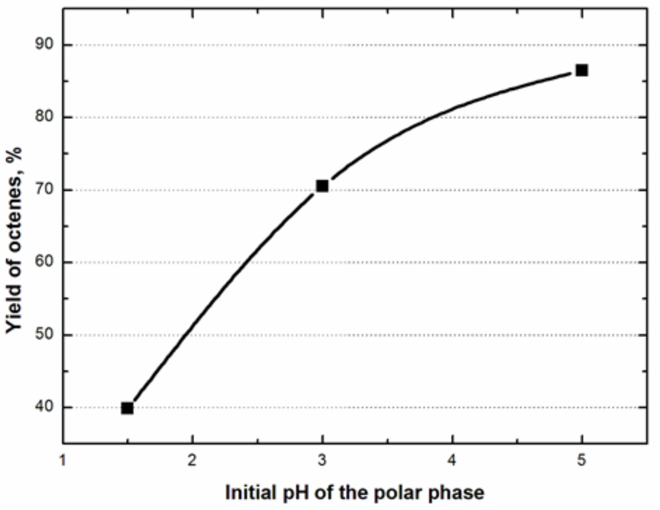

Fig. 10**.** Yields of isobutene oligomers obtained with the isobutene to glycerol molar ratio of 1.5 and for different initial *p*H values of the polar phase in presence of ROT 1

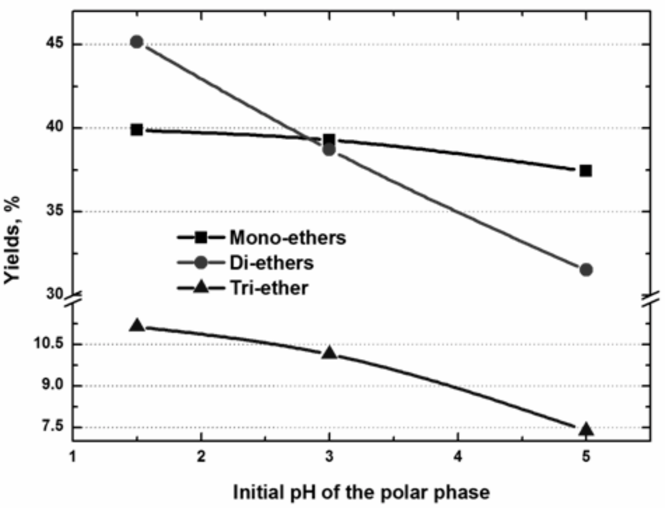

Fig. 11**.** Yields of ethers for isobutene to glycerol molar ratio of 1.5 and different initial *p*H values of the polar phase in presence of ROT 1.

the polar phase, resulting in higher yields of ethers, as shown in figure11.

Conclusions

Although we do not have a direct evidence for the formation of an emulsion between isobutene and glycerol in the presence of the emulsifiers during the reaction under the conditions used in our experiments, we have unambiguously observed that ROT 1 stabilizes the emulsion formed in a glycerol – olefin mixture, and that the performance of the etherification process was significantly improved by adding an appropriate emulsifier in the reaction environment. Therefore, we conclude that emulsifiers with similar structures may lead to quite different results and selection of an optimal emulsifier should be considered in order to achieve the best performance for glycerol etherification with isobutene.

Using an efficient emulsifier, ROT 1, and screening several reaction parameters, we proposed that both etherification and oligomerization reactions occur in the polar phase at the catalyst surface where isobutene and glycerol molecules compete for the same active sites of the catalyst, with isobutene molecules likely winning against glycerol, mono- and di-ether molecules. Reactive intermediary species resulting from the isobutene, glycerol, mono- or di-ethers with the catalyst active sites, always react with dissolved isobutene in the polar phase. Along these lines, we conclude that improving the mass transfer between the polar and the nonpolar phases of the reaction mixture can improve the overall performance of the process. However, increasing the isobutene concentration in the polar phase beyond an optimal value leads to lower selectivity of isobutene to ethers and lower values of the glycerol conversion. Therefore, the optimal reaction parameters should be determined in correlation with a reaction system that allows fine tuning of the isobutene concentration in the polar phase through controlling the rate of the mass transfer between the phases in the reactor.

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