The Influence of the Character of Emulsifiers on the Performance of $H_4SiW_{12}O_{40} . 30H_2O$ Heteropolyacid Catalyst in Glycerol Etherification with Isobutene

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The heteropolyacid $H_4SiW_{12}O_{40}.30H_2O$ proves to be a performant catalyst for glycerol etherification with isobutene, showing good conversion for both reagents and high yields to ethers. To improve the performance of the process different types of emulsifiers were used for a more intense mass transfer between the two liquid phases formed by the reactants. The experimental study on glycerol etherification with isobutene was conducted over heteropolyacid $H_4SiW_{12}O_{40}.30H_2O$ catalyst in the presence of three types of emulsifiers: amphoteric ammonium quaternary salt C_{19}, non-ionic ethoxylated alcohol C_{12}-C_{14}, and cationic Dinoram S. All emulsifiers used form direct emulsions. An increase in the concentration of the cationic emulsifier leads to a steady decrease in the yields and selectivity to desired products in spite of the higher conversion of both reagents. The non-ionic emulsifier forms a stable emulsion, independent on the pH of the reaction mixture leading to higher yields in desired products at lower concentrations. Glycerol and isobutene conversions had higher values with the amphoteric ammonium quaternary salt C_{19} and non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifiers. The distribution of the reaction products is significantly modified by the increase of the concentration of ammonium quaternary salt C_{19} and ethoxylated alcohol C_{12}-C_{14} emulsifiers, towards the increase of the yields to di- and tri-ethers.

Keywords: glycerol etherification, ethoxylated alcohol C_{12}-C_{14}, ammonium quaternary salt, cationic emulsifier, direct emulsion.

Manufacturing of biodiesel at industrial scale by transesterification of vegetable fats with methanol, process in which glycerol results as a by-product, is the most frequently used process to produce alternative diesel fuels. This suggests that ways to convert glycerol into more valuable products are highly desirable.

Among others, one possible conversion route is the glycerol etherification with olefins. Many of the recent studies were dedicated to glycerol etherification with isobutene using different catalysts, such as sulfonic acids supported on ordered mesoporous molecular sieves, zeolites, ion exchange resins and homogenous acid catalysts [1-6]. By reacting glycerol with isobutene a range of ethers may be obtained, such as mono-, di-, and tri-tert-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively). The results observed in glycerol etherification experiments with isobutene using a strongly acidic cross linked ion exchange resin Amberlyst 35 catalyst demonstrated high conversions for both reagents and good yields in desired products [1]. Other researchers have investigated the direct synthesis of C8-chain mono- and di-ethers of glycerol and a number of renewable glycols in the reaction of glycerol with 1-octene. Reactions were performed in a solventless system in liquid phase using various commercial solid acid catalysts such as zeolites (H-Beta, H-Y, H-ZSM-5) and ion-exchange resin (Amberlyst 70), and showed good yields in the desired products and high conversions for both reactants [7].

Heteropolyacids possess both acid and redox properties, thus promote a variety of acid-catalyzed reactions, as well as catalytic oxidation reactions in both homogeneous and heterogeneous systems; for example, the synthesis of ethyl acetate from ethylene and acetic acid, and the oxidation of ethylene to acetic acid, were accelerated using supported HPA catalysts [8]. They can also be used in petrochemical synthesis for the hydration of alkenes, synthesis of ethers and esters, and for the isomerization of alkanes [9].

Among other types of catalysts used for the etherification of glycerol with isobutene, the liquid heteropolyacid HSiW is insoluble in higher ethers of glycerol and, thus, tend to promote isobutene oligomerization. As a result they have a strong tendency to impeding the formation of TTBG during the initial stage of glycerol conversion; also there is a quite high affinity of isobutene for the Keggin anion due to the protonation of isobutene and the formation of the alkoxy state bound to Keggin anion. These bound alkoxy-species may couple with a next isobutene molecule producing dimeric species [10].

However, in a heterogeneously catalyzed reaction, the reactants must come in contact with the active sites at the catalytic surface, and this condition is somewhat more difficult to achieve with reaction taking place in the liquid phase, especially when the reactants do not dissolve each other. This is precisely the case with the reaction between glycerol – a polar, viscous liquid – and isobutene – a nonpolar liquid, under these reaction conditions. These liquids form two phases with very low reciprocal solubility, thus, independent on the distribution of catalyst particles between the two liquid phases, one of the reactants has a very low concentration at the catalyst surface. Moreover, if the catalyst is distributed predominantly into the nonpolar phase, under the reaction conditions used isobutene molecules react with each other producing isooctene oligomers, an unwanted byproduct.

One possible way to intensify the mass transfer between the two liquid phases is to increase the contact surface between the two liquid phases. The most effective

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mean to achieve this is to form an emulsion where the glycerol is the continuous phase and the isobutene is the dispersed phase. Such an emulsion can be obtained by stirring, but the resulting emulsion is unstable and results quickly into two liquid phases as stirring ceases.

The most important parameters affecting the stability of an emulsion is the size of the droplet, and the droplet size distribution in the populations. These are influenced by the emulsification procedure and by the type and amount of emulsifier used. When the drops are formed as an effect of mechanical stirring, the presence of an emulsifier reduces the interfacial tension between the two liquids: glycerol and isobutene.

The non-ionic emulsions are stable independently on the pH of the reaction mixture, thus, the non-ionic emulsifier forming direct emulsions favours total conversion of the reagents. However, for the cationic emulsifier forming cationic emulsions, the *p*H of the reaction mixture is essential to favoring formation of direct emulsions, and correction to strong acid reaction environment is required [11]. There were few experiments of glycerol etherification with isobutene performed in the presence of an imidazolinic cationic emulsifier ROT 1 reported in the literature, where the performance of the etherification process has been proven to be strongly dependent on the mass transfer between the two liquid phases. The *p*H has also influenced the ionization degree of the emulsifier, such that a highly ionized emulsifier, corresponding to *p*H=1.5, favours obtaining of direct emulsions with droplet diameter distribution that improves significantly the mass transfer between the two liquid phases, and impedes the base emulsifier molecules to blocking the acid sites of the catalyst [1].

To the best of our knowledge, there are no reports in the literature on the effects of the amphoteric ammonium quaternary salt ($C_{19}H_{42}NBr$), non-ionic ethoxylated alcohol C_{12}-C_{14} with 7 ethylene-oxide groups and cationic Dinoram S emulsifiers on the glycerol etherification with isobutene. In this contribution we have studied the performance of the solid heteropolyacid $H_4SiW_{12}O_{40}$.$30H_2O$ catalyst in the glycerol etherification reaction with isobutene, both in the absence of emulsifiers and in presence of three types of emulsifiers – cationic, non-ionic and amphoteric, in order to identify the best performing conditions for this catalyst. Reactant conversions, product yields and selectivity were used to characterize the performance of the glycerol etherification process with isobutene.

Experimental part

Raw materials

Ethoxylated alcohol C_{12}-C_{14} with 7 ethylene-oxide groups and 90.0 % active phase used as emulsifier, also the amphoteric ammonium quaternary salt emulsifier (N-cetyl N, N, N-tri-methyl ammonium bromide) or $C_{19}H_{42}NBr$, were provided by ICECHIM Bucharest. The cationic emulsifier (N-tallow propylene diamine) or Dinoram S was provided by Ceca Chemicals. The solid heteropolyacid $H_4SiW_{12}O_{40}$.$30H_2O$ catalyst was purchased from Sigma Aldrich. The 99.0 % purity isobutene purchased from Linde and analytical glycerol provided by Chimopar were the reagents used for all the catalytic tests.

Etherification experiments

The solid heteropolyacid $H_4SiW_{12}O_{40}$.$30H_2O$ catalyst was tested in the glycerol etherification with isobutene to yield a mixture of mono-, di-, and tri-tert-butyl glycerol ethers (MTBG, DTBG, and TTBG, respectively). These experiments have been performed in a 600 mL stainless steel Berghoff autoclave, equipped with mechanical stirring and electrically heated, with automatic temperature control. The mixture of glycerol (130.0 g), isobutene (molar ratio isobutene/glycerol of 3/1), emulsifier (0.0, 0.1, 0.4 and 0.7 wt %) and catalyst (5.0 wt %) were heated at 353 K for 5 h under stirring at 1200 rot/min. The concentrations of the catalyst and emulsifier were referenced to the amount of glycerol. The experiments with the cationic emulsifier Dinoram S were conducted with a *p*H correction of the glycerol phase, by drop-wise adding of phosphoric acid 85.0 vol % till the *p*H of the reaction mixture reached 1.5. For the experiments performed in the presence of ethoxylated alcohol and ammonium quaternary salt emulsifiers, the reaction has been performed without *p*H correction. Characterization of the reaction products was performed by gas-chromatography, using an instrument from Agilent Technologies with FID detector, equipped with DB-WAX polar column of 30 m length and 0.32 mm inner diameter. The chromatographic column was operated at 313-493 K with nitrogen as carrier gas. Glycerol and isobutene conversions (X_G, X_{IB}), yields to ethers ($\eta_{ether\ i}$) and selectivity of isobutene to ethers ($S_{ether\ i}$) were calculated based on the chromatographic analyses using the following equations, respectively:

$$X_G = \frac{moles\ of\ glycerol\ converted}{starting\ moles\ of\ glycerol} * 100$$

$$X_{IB} = \frac{mol\ of\ isobutene\ converted}{starting\ moles\ of\ isobutene} * 100$$

$$\eta_{ether\ i} = \frac{moles\ of\ glycerol\ converted\ to\ ether\ i}{starting\ moles\ of\ glycerol} * 100$$

$$S_{ether\ i} = \frac{moles\ of\ isobutene\ converted\ to\ ether\ i}{starting\ moles\ of\ isobutene} * 100$$

Results and discussions

The catalytic test of glycerol etherification with solid heteropolyacid $H_4SiW_{12}O_{40}$.$30H_2O$ without emulsifier shows good conversions for reagents (93.6 % for glycerol and 100.0 % for isobutene), high yields to ethers (around 38.1 % of MTBG, 52.2 % of DTBG and 3.3 % of TTBG) and good values for isobutene selectivity in ethers (around 12.9 % of MTBG, 17.6 % of DTBG and 1.1 % of TTBG). These results were used as reference for all experimental runs in presence of the heteropolyacid and emulsifiers, and, at the same time, are showed in all figures.

Isobutene selectivity to ethers (fig. 1 (A)) shows decreasing values with increasing of the concentration of the cationic emulsifier Dinoram S, and also, steady increases when the amount of the non-ionic ethoxylated alcohol C_{12}-C_{14} or amphoteric ammonium quaternary salt C_{19} emulsifiers increase. Isobutene selectivity to ethers shows higher values for the experiments performed with emulsifiers compared to that obtained without them, suggesting that the emulsifying process favours the etherification reaction and also, promotes a more effective contact between isobutene and the catalyst particles most likely due to the decrease of the viscosity of the glycerol phase. Isobutene selectivity to oligomers (fig. 1 (B)) shows lower values for the experiments performed in presence of emulsifiers compared to that obtained without them. The values of isobutene selectivity to oligomers show different behaviour in presence of emulsifiers. When the cationic emulsifier Dinoram S is used the isobutene selectivity to oligomers shows a faster decrease by 24 %

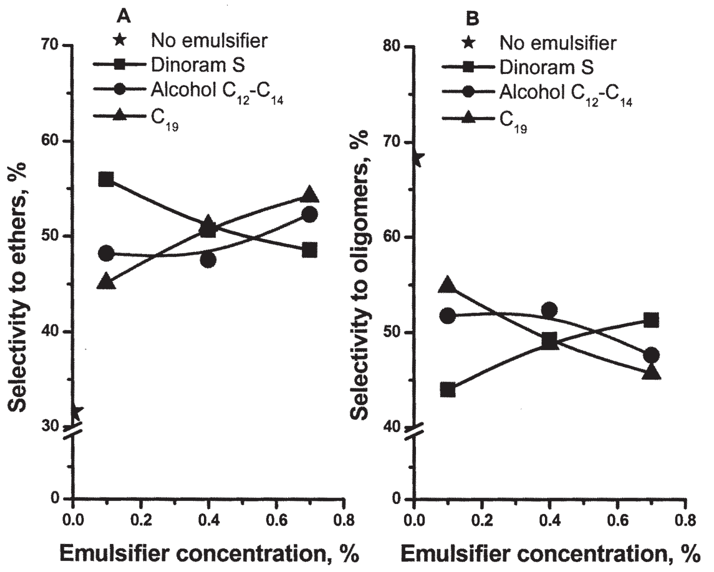

Fig. 1.The influences of the emulsifiers on the selectivity of isobutene to ethers (A) and oligomers (B)

compared to the value obtained without emulsifier, followed by an increase when the amount of cationic emulsifier increases. When using the non-ionic ethoxylated alcohol C_{12}-C_{14} or amphoteric ammonium quaternary salt C_{19} emulsifiers, the isobutene selectivity to oligomers shows a steady decrease by 13-15 % compared to the value obtained without emulsifier, followed by decreasing with the concentration of the emulsifiers.

The cationic emulsifier Dinoram S favours obtaining higher conversion for glycerol, most likely due to the formation of direct emulsions (fig. 2 (A)). Glycerol conversion shows decreasing values when the amount of the cationic emulsifier Dinoram S increases. Isobutene conversion (fig. 2 (B)), however, shows a more pronounced decrease associated to the increase in the amount of cationic emulsifier. A possible explanation for these results is a negative influence produced by the increase of the concentration of the cationic emulsifier added to the reaction mixture, which suggests a faster increase of the concentration of the isobutene molecules dissolved in the glycerol phase, thus favouring the oligomerization reaction and not isobutene conversion to ethers (as shoed in fig. 1 (B)). The glycerol conversion (fig. 2 (A)) increases with the concentration of the non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifier. Higher glycerol conversion (around 98.6 % at 0.7 % emulsifier) compared to the values obtained without using emulsifier is observed. The isobutene conversion (fig. 2 (B)) is constant near 100 % for all experiments with non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifier. The non-ionic emulsifier forms stable direct emulsion independent on the *p*H of the reaction mixture. Catalyst particles are readily available to promoting glycerol etherification reactions because of the decrease of the viscosity of the glycerol phase as a result of the emulsification process. The amphoteric ammonium quaternary salt C_{19} emulsifier favours obtaining maximum values for isobutene conversion (fig. 2 (B)) and, the glycerol conversion is also higher (even at 0.1 % emulsifier) and it increases with the concentration of the ammonium quaternary salt emulsifier (fig. 2 (A)). The amphoteric ammonium quaternary salt C_{19} emulsifier forming direct emulsion that favors the total conversion of the glycerol and isobutene, also provides a good contact between isobutene drops and the catalyst particles. Thus, the amphoteric ammonium quaternary salt C_{19} and non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifiers have positive effects for conversions of both reagents, while the cationic emulsifier Dinoram S has a negative effect.

The best results are obtained when using 0.7 % ammonium quaternary salt C_{19} emulsifier (fig. 3) which gives the lowest yield value to mono-ether (about 9.7 % of MTBG). The highest yield to mono-ether (about 48.6 % of MTBG) is obtained at 0.7 % cationic emulsifier Dinoram S. By adding emulsifier the yield values to mono-ether show different behavior compared to that obtained without emulsifier (about 38.1 %). When cationic emulsifier Dinoram S is added, yields to mono-ether are decreasing to lower values (about 14.0 % of MTBG at 0.1 % emulsifier). By increasing the amount of cationic emulsifier Dinoram

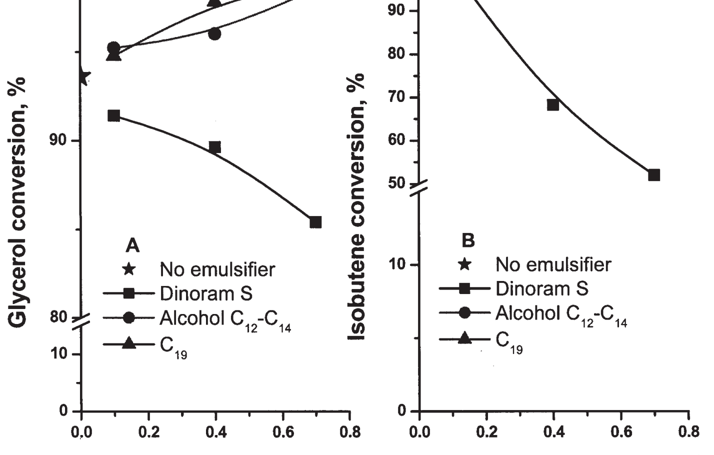

Fig. 2.The influences of the emulsifiers on the glycerol (A) and isobutene (B) conversions

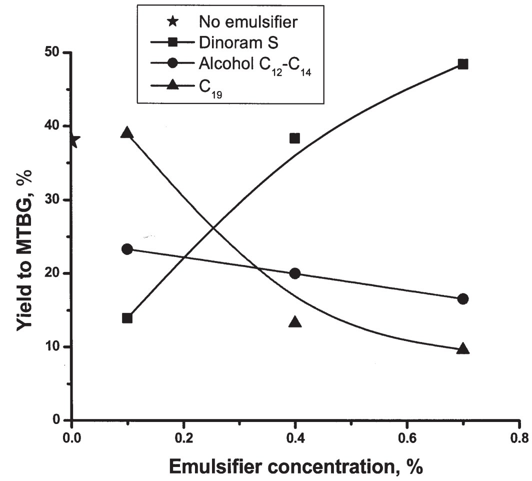

Fig. 3.The influences of the emulsifiers on the yield of glycerol in MTBG

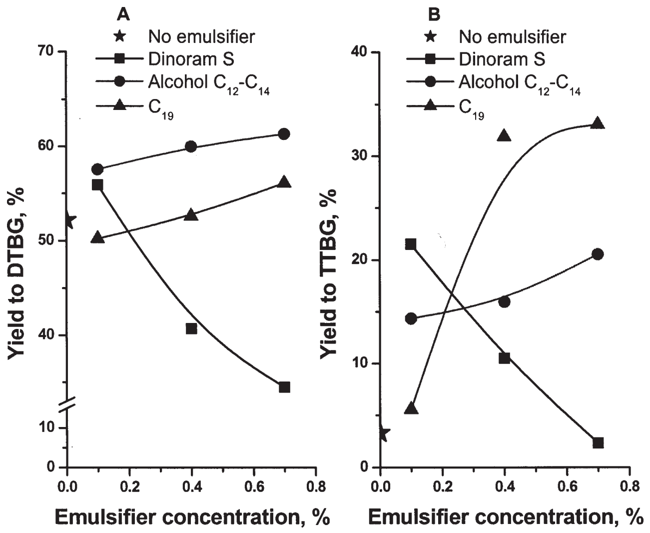

Fig. 4.The influences of the emulsifiers on the yield of glycerol in DTBG (A) and TTBG (B)

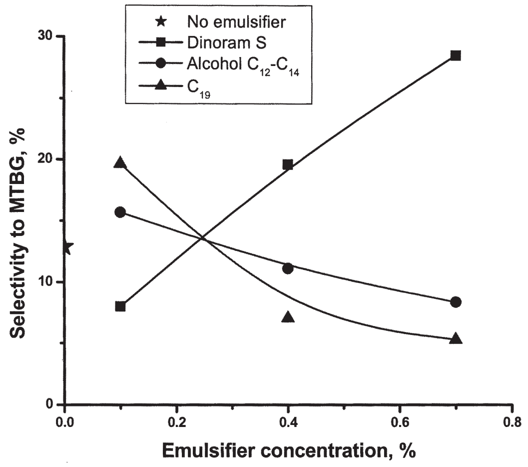

Fig. 5.The influences of the emulsifiers on the selectivity of isobutene in MTBG

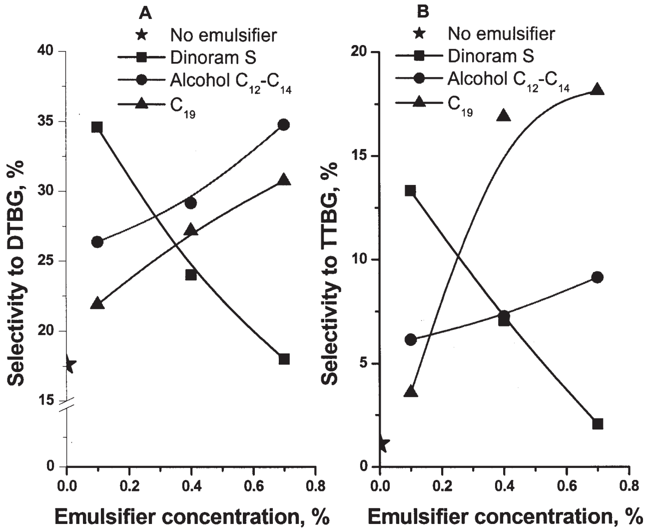

Fig. 6.The influences of the emulsifiers on the selectivity of isobutene in DTBG (A) and TTBG (B)

S, the yield to mono-ether increases significantly (about 48.6 % of MTBG at 0.7 % emulsifier). When non-ionic ethoxylated alcohol C_{12}-C_{14} and ammonium quaternary salt C_{19} emulsifiers are used yield values to mono-ether decrease to lower values for the alcohol C_{12}-C_{14} (about 23.3 % of MTBG at 0.1 % emulsifier) and there is a small increase for the C_{19} emulsifier (about 39.0 % of MTBG at 0.1% emulsifier). The influence of the non-ionic ethoxylated alcohol C_{12}-C_{14} and ammonium quaternary salt C_{19} emulsifiers is positive for the yield to mono-ether, that is decreasing with increasing the concentration of the emulsifier. The non-ionic emulsifier is a strong acid emulsifier which leads to higher yields in desired products at lower concentration. Because this emulsifier favours formation of direct and non-ionic emulsions, higher selectivity in ethers was achieved with this emulsifier by increasing the concentration of isobutene molecules in the glycerol phase surrounding the catalyst particles.

The best results are obtained when using 0.7 % ammonium quaternary salt C_{19} emulsifier (fig. 4) which results in the highest yields to di- and tri-ethers (about 56.1 % of DTBG and 33.1 % of TTBG); this also true for non-ionic ethoxylated alcohol C_{12}-C_{14} at 0.7 % concentration emulsifier (around 61.4 % of DTBG and 20.6 % of TTBG). By adding emulsifier the yield values to di- and tri-ethers show different behaviour compared to those obtained without emulsifier (about 52.2 % of DTBG and 3.3 % of TTBG). When the cationic emulsifier Dinoram S is added, the yield values to di- and tri-ethers increase, followed by steady decrease when the concentration of emulsifier increases at an attenuated slope for high emulsifier concentrations. Even if Dinoram S is a cationic emulsifier forming direct cationic emulsions, the increase of the concentration of the emulsifier shows a steady decrease in the yields to desired products. When ammonium quaternary salt C_{19} emulsifier is employed the yields to di-ether (fig. 4 (A)) decrease to lower values (about 50.2 % at 0.1 % emulsifier) followed by an increase with increasing the concentration of emulsifier; also, by increasing the amount of C_{19} emulsifier the yield to tri-ether is increasing significantly from 5.6 % at 0.1 % emulsifier to 31.9 % at 0.4 % emulsifier (fig. 4 (B)). The influence of the non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifier is positive; the yields of di- and tri-ethers increase with increasing the concentration of the emulsifier.

A similar behaviour is observed for the isobutene selectivity to mono-ether: the lowest selectivity value for mono-ether (about 5.3 % of MTBG) is obtained when using 0.7 % ammonium quaternary salt C_{19} emulsifier (fig. 5). The highest selectivity to mono-ether (about 28.6 % of MTBG) is obtained at 0.7 % cationic emulsifier Dinoram S. A faster enhancement for the isobutene selectivity to mono-ether is observed with increasing the concentration of cationic emulsifier Dinoram S. The smaller increase followed by a constant decrease for selectivity to mono-ether is observed when non-ionic ethoxylated alcohol C_{12}-C_{14} and ammonium quaternary salt C_{19} emulsifiers are added compared to the results obtained without emulsifier (about 12.9 % of MTBG), since they assured obtaining a higher conversion to the desired ethers.

A similar behaviour with the yield values to di- and tri-ethers is observed; higher values for the isobutene selectivity to di- and tri-ethers (around 30.8% of DTBG and 18.2% of TTBG) when using 0.7 % ammonium quaternary salt C_{19} emulsifier, and for non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifier (around 34.8 % of DTBG and 9.1% of TTBG). A constant increase for the isobutene selectivity to di- and tri-ethers is observed with increasing the concentration of ammonium quaternary salt C_{19} and non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifiers compared to the results obtained without emulsifier (around 17.6% of DTBG and 1.1 % of TTBG). The isobutene selectivity to ethers shows higher value for di- and tri-ethers (around 34.6 % of DTBG and 13.3% of TTBG) when using 0.1% cationic emulsifier Dinoram S, followed by a significant decrease to 18.1% of DTBG and 2.1% of TTBG at 0.7 % emulsifier concentration.

Conclusions

The catalytic test without emulsifier shows good conversions for reagents and high yields to ethers. Higher values for the isobutene selectivity to ethers were obtained for the experiments performed in the presence of emulsifiers compared to those obtained without them, suggesting that the emulsifying process favours the glycerol etherification reaction. The cationic emulsifier Dinoram S favored obtaining higher conversion of the reagents most likely because it forms direct emulsions in the acid environment of the reaction mixture and, the increase of the concentration of the emulsifier leads to a steady decrease in the yields and selectivity to the desired products. The non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifier forming stable direct emulsions independent on the *p*H value of the reaction mixture, also favours high yields to the desired products at lower concentration. The amphoteric ammonium quaternary salt C_{19} emulsifier forming direct emulsion favors total conversion of glycerol and isobutene, also providing the highest yields to the desired products, di- and tri-ethers (about 56.1% of DTBG and 33.1% of TTBG) at 0.7 % concentration. This makes the amphoteric ammonium quaternary salt C_{19} emulsifier the most efficient emulsifier for the glycerol etherification with isobutene. The distribution of the reaction products is significantly influenced by increasing the concentration of ammonium quaternary salt C_{19} and non-ionic ethoxylated alcohol C_{12}-C_{14} emulsifiers, towards the increases of the yields to di- and tri-ethers.

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