Glycerol Etherification with Isobutene in the Presence of Nonionic Emulsifiers

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Converting glycerol into value added products presents opportunities for the biodiesel price evolution. One of the alternatives of recovery is the production of glycerol ether with isobutene, compounds with suitable properties for use as components or additives for fuel. The improvement of the etherification process can be achieved by improving mass transfer between glycerol and hydrocarbon phases by emulsifying the reaction mixture. This aspect was evidenced by performing glycerol etherification with isobutene without emulsifier and in presence of a two nonionic emulsifiers, nonylphenol ethoxylated with 9 ethylene oxide molecules and lauryl alcohol ethoxylated with three ethylene oxide molecules. Etherification experiments were conducted in the presence of an acid catalyst type cationic ion exchange resin, Purolite CT 275. The yields to di- and triethers, products with low polarity suitable as components for diesel fuels, is significantly modified in presence of the nonionic emulsifiers.

Keywords: glycerol etherification, isobutene, ion exchange resin, nonionic emulsifier

The increase production of biodiesel has aroused concerns about the use of resulting glycerol as a byproduct from its manufacture. Tendency to expand the production of biodiesel will cause increased production of glycerol, so it will be difficult to identify eligible variants for capitalization thereof. Converting glycerol into value added products presents opportunities for the biodiesel price evolution. At the same time to reduce the world’s dependence towards non-renewable resources is crucial to be developed processes based on biomass that can be the alternative of getting chemicals from crude oil.

One of the alternatives of recovery is the production of oxygenated compounds that have suitable properties for use as components or additives for fuel by glycerol etherification with lower alcohols (e.g., methanol or ethanol) or alkenes (i.e. isobutene). By reacting of glycerol with isobutene can be obtained 1- and 2-t-butoxy-glycerol (MTBG), 1,2- and 1,3-di-t-butoxy-glycerol (DTBG), and 1,2,3 tri-t-butoxy-glycerol (TTBG).

When glycerol is etherified with isobutene in order to obtain additives for fuels is necessary that most or all of the hydroxyl groups of the glycerol molecule to react in order to ensure a good solubility in the hydrocarbon medium. The process takes place in the presence of acid catalysts. There have been carried out many studies of the glycerol etherification with isobutene using various catalysts such as zeolites, ion exchange resins and homogeneous acid catalysts [1-4]. Isobutene oligomerization in hydrocarbons C8, C12 and C16 may occur in the presence of acid catalysts. Instead glycerol polymerization to polyglycerols occur only in the presence of basic catalysts. Each other solubility of the two reactants is very low. Thus based on equilibrium calculations, at the stoichiometric initial condition (molar ratio of isobutene / glycerol = 3:1), glycerol phase equilibrium mixture contains less than 3% mol isobutene and isobutene phase contains not at all glycerol [5].

The etherification process may be accompanied by dealkylation reactions that are not observed when the process arising in the presence of H-BEA type zeolite. [6]

According to the process evolution, products are accumulated into a phase or into the other, depending on their solubility. Thus monoethers are accumulated in the polar glycerol phase while diethers, triethers and C8-C16 hydrocarbons are accumulated in nonpolar hydrocarbon phase.

Improving mass transfer and hence the contacting of the two reactants and the reaction intermediates can be achieved by emulsifying the two phases, respectively glycerol phase and isobutene phase. In a recent paper is proposed using cationic emulsifiers for improving mass transfer between the two phases [7]. Acid medium used for emulsification using cationic emulsifiers may favor the amplification of isobutene oligomerization.

Another class of emulsifying compounds which may favor contacting the two phases in order to improve the processed of glycerol etherification with isobutene diminishing oligomerization side reactions is the nonionic emulsifiers. In order to evaluate the performance of this emulsifiers class were selected two nonionic emulsifiers whose hydrophilic - hydrophobic balance is different, first, nonylphenol ethoxylate with 9 ethylene oxide molecules is soluble in water and favor the formation of a directly emulsion, while the second, respectively lauryl alcohol ethoxylated with 3 ethylene oxide molecules is oleo-soluble and favor the formation of an indirectly emulsion. Another difference between the two emulsifiers is that emulsifiers type fatty alcohol ethoxylates shows a higher dispension molecular weight than those of ethoxylated nonylphenol type and thus favors obtaining an emulsion with a wider droplet size distribution.

Experimental part

The experiments were performed in a 600 mL stainless steel Berghoff autoclave equipped with mechanical stirring. The autoclave is electrically heated, with automatic temperature control. Reagent grade glycerol provided by Aldrich and 99% purity isobutene purchased from Linde were the agents used for all the experimental runs. The catalyst selected is a macroporous, strongly acidic,
polymeric catalyst PUROLITE CT 275, with a concentration of sulphonatic groups higher than 5.2 meq/dry g, a specific surface area 25 - 35 m\(^2\)/dry g and a median pore diameter 600 - 750 Å. Prior to use, the catalyst was washed with methanol to remove water, then dried. Swelling of catalyst was achieved in reactor by contacting with the glycerol used to perform the experiment. The concentration of the catalyst with respect to the amount of glycerol loaded in the reactor was 5 wt % for all experiments performed. The stirring rate was maintained at 1300 rot/min for each experiment.

The emulsifiers used in the study were nonylphenol ethoxylated with 9 ethylene oxide molecules, Empilan NP 9 (noted NF 9) and lauryl alcohol ethoxylated with three ethylene oxide molecules, KBE 2.7 (noted Empilan) provided by Huntsman Corporation. Nonionic emulsifier concentration with respect to the amount of glycerol and isobutene had values between 0.17 and 0.35 %.

All experimental runs were performed for 5 h at 60-80°C and at isobutene/glycerol molar ratio of 1.5-2.5/L. The pressure in the reactor was monitored continuously during the whole duration of each experiment. The analyses of starting materials and reaction products were 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 between 20-220°C, with nitrogen as carrier gas. The chromatographic analyses of reaction products have demonstrated the presence of two isomers for the glycerol mono-ether (1- and 2-t-butoxi-glycerol) and the glycerol di-ether (1,2- and 1,3-di-t-butoxy-glycerol) and of the tri-ether (1,2,3-tri-t-butoxy-glycerol). Conversion of glycerol, and yields to mono-ethers, di-ethers, tri-ether of glycerol and isooctenes were calculated based on the material balance for each experiment.

Results and discussions
The influence of nonionic emulsifier type

The nonionic emulsifier influence of the glycerol etherification process with isobutene was studied in comparison with the process carried out without emulsifiers. The temperature was 80°C, the isobutene/glycerol molar ratio was 1.5 and the concentration of non-ionic emulsifier was 0.17 wt %. Efficiency of etherification process in the presence of nonionic emulsifier is evidenced by greater conversion of glycerol in the presence of both emulsifiers tested, compared to the case in which is not used emulsifier (fig. 1). Efficiency of the two emulsifiers is appropriate in this regard.

Yield in ethers shows a different variation when the reaction proceeds in the presence of a nonionic emulsifier or in its absence. Thus in the presence of the two emulsifiers selected, triethers yield is lower than when the reaction proceeds in the emulsifiers absence, while the yield in diethers increases significantly when using emulsifiers; efficiency of the two emulsifiers is close from this point of view (fig. 2).

Influence of nonionic emulsifier content

The study concerning the influence of nonionic emulsifier content on the etherification process was carried out with NF 9 emulsifier at concentrations up to 0.35%. The temperature was 80°C and the molar ratio isobutene/glycerol was 1.5/L.

The conversion of glycerol increased with the concentration of the emulsifier up to a concentration of 0.2% and then remains constant, while the conversion of isobutene varies with a maximum located at a concentration of emulsifier of 0.1% (fig. 3).

Glycerol monoethers yield had relatively constant values for the concentrations domain of the emulsifier used (fig. 4). From the same figure it is observed that the diethers yield increases at the emulsifier concentration lower than 0.1% and the triether yield decreased in the emulsifier presence.
Isobutene selectivity to ethers, depending on the NF 9 emulsifier concentration, varies by curves similar to those concerning yield glycerol ethers (fig. 5).

Diisobutene concentration from effluent fell sharply at a concentration of NF 9 emulsifier of approximately 0.1% and remained at an approximately constant value for the range of emulsifier concentrations tested (fig. 6).

Efficiency of NF 9 emulsifier was evidenced by presenting the half-life of the pressure (fig. 7). Note that the rate of isobutene consumption has lower values in the absence of emulsifier and at its high concentrations; performance of the process increases at low levels of emulsifier concentration (0.1%).

The influence of temperature

Influence of the temperature on the process of etherification in the presence of a nonionic emulsifier was studied with EMPILAN emulsifier. The study was conducted at the temperature range of 60-80°C in a molar ratio of isobutene / glycerol 1.5 / 1 and an emulsifier content of 0.1 wt %.

Glycerol conversion increases by over 30% with increasing temperature (fig. 8). The same growth shows the isobutene conversion to ethers, as shown in the same figure.

The growth of glycerol conversion is given by the increase in mono- and di-ethers yields (fig. 9). Thus results may be caused by the increase of isobutene concentration solubilized in glycerol phase with increasing temperature and by improving mass transfer between phases, probably favored by reduction of glycerol viscosity.

As seen in figure 10, the dimerization process of isobutene in the presence of nonionic emulsifier is significantly influenced by temperature. Thus, diisobutene content increase significantly with temperature. This increase is probably due to the higher value of the activation energy in the oligomerization reaction, aspect highlighted by other authors [2], and by growth of isobutene solubilization in glycerol phase with the increase of temperature.

The influence of the isobutene / glycerol molar ratio in the presence of non-ionic emulsifier

The study was conducted at values of the molar ratio isobutene / glycerol of 1.5 - 2.5 at 80°C and at the emulsifier content of 0.1 wt %. The influence of molar ratio isobutene
glycerol on the glycerol conversion in the presence of the two non-ionic emulsifiers, NF 9, respectively Empilan, is shown in figure 11. The effect of the two emulsifiers is similar, the variation curve of glycerol conversion with molar ratio of isobutene/glycerol overlapping and showing a negative slope variation. When the process occurs in the absence of emulsifiers the glycerol conversion increase with molar ratio of isobutene/glycerol, probably due to favorable modification of the size distribution of the emulsion droplets of the discontinuous phase.

Monoethers yield decreases with increasing molar ratio isobutene / glycerol both in the presence and in the absence of emulsifiers (fig. 12). Slope of the curve variation is greater in the emulsifiers absence and has a value close when the reaction proceeds in the presence of both emulsifiers. From the same figure it is observed that yield in monoethers has higher values in the presence of emulsifier type fatty alcohol ethoxylate than in the presence of emulsifier type nonylphenol ethoxylate.

Diethers yield decreases with increasing isobutene/glycerol molar ratio in the presence of two emulsifiers (fig. 13) while in the absence of emulsifiers it grows. The slope of variation has values close for the two emulsifiers, yield in diethers showing higher values in the presence of emulsifier type nonylphenol ethoxylate.

Triether yield decreases with increasing molar ratio isobutene/glycerol in the presence of both emulsifiers (fig. 14) while in the absence of emulsifiers it grows. Slope variation has similar values when the reaction proceeds in the presence of both emulsifiers, the yield in triether showing higher values in the presence of emulsifier type fatty alcohol ethoxylate.

Diisobutene concentration increases with the molar ratio of isobutene /glycerol both in the presence and in the absence of two emulsifiers after a slope appropriate (fig. 15). Note that diisobutene concentration drops by around 30% when the etherification occurs in the presence of emulsifiers at a molar ratio isobutene / glycerol of about 1.5/L.

Conclusions
The presence of two nonionic emulsifiers, ethoxylated nonylphenol and ethoxylated fatty alcohol type on the glycerol etherification with isobutene, over the catalyst type ion exchange Purolite CT 275, at temperatures up to 80°C improves glycerol conversion probably by increasing mass transfer.

The distribution of reaction products has changed, so the yield in diethers increases and the yield in mono-and triethers decreases in the presence of the two nonionic emulsifiers.
Diisobutene content diminished considerably in the presence of the two nonionic emulsifiers.

The performance of etherification process of glycerol with isobutene were assessed by comparing the half-life of the pressure; the presence of emulsifiers at a optimal concentration increases the consumption rate of isobutene.

References

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