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Catalytic production of oxygenated additives by glycerol etherification[1]

Research Article

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Abstract: In this work the etherification reaction of glycerol with isobutene (IB) and *tert*-butyl alcohol (TBA) has been studied with the aim of preparing mixtures with high content of *poly*-substituted ethers. The results obtained using solid acid catalysts have shown that the reaction with IB proceeds at a high rate but the formation of undesired *di*-isobutene (DIB) represents a serious problem when catalysts with high density of acid sites, such as Amberlyst, are used. When using TBA as a reactant, the main problem is the formation of water that, due to thermodynamic reasons, prevents the formation of *poly*-substituted ethers regardless of the catalyst used. Some preliminary experiments carried out with a water permselective tubular membrane have demonstrated that the yield of *poly*-substituted ethers significantly increases once water was selectively removed from the reaction medium by recirculation of the gas phase.

Keywords: Glycerol conversion • Diesel additives • Etherification reaction • Solid acid catalysts • Water membrane
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1. Introduction

In the recent years biodiesel has proved its value as a fuel for diesel engine due to its prominent superiority over the petroleum diesel in terms of health and environment as well as good engine performance (*i.e.*, high enhance lubricity and high cetane number). The demand for biodiesel has rapidly increased, especially in the European Union [1]. Nevertheless, the increased production of biodiesel inevitably produces a surplus of glycerol since it is the major by-product (~10 wt.%) of the transesterification reaction of vegetable oils; one mol of glycerol is being produced for every 3 mol of methyl esters [2]. Therefore, although glycerol itself has many commercial applications in cosmetic and pharmaceutical industries, the development of new efficient ways of converting it to the added-value products is necessary to validate the eco-sustainability and economics of the global biodiesel process [3,4]. Among different approaches proposed recently, the possibility of producing oxygenated additives by either etherification

[5-7] or esterification reaction [8,9] has received great attention. This is due to the benefits of the oxygenated additives in terms of both environmental compliance and efficiency of engines [10,11]. Particularly, oxygenated compounds could assist in octane rating increment and in combustion quality by reducing particulate emission and carbon monoxide production. Based on that, glycerol derived ethers have been recently considered as potential additives for diesel fuel since they have compatible physico-chemical properties in terms of flash point, viscosity, cetane number, *etc*. [12]. In particular the *poly*-substituted ethers (*di*- and *tri*-ethers) are very suitable as diesel additives due to their good properties of blending with petroleum fuels and their cetane number acceptable for diesel engine application [10]. As additives they improve engine performance [13,14], perform well in cold weather, decrease fuel viscosity and reduce emission of contaminants in fumes and particulate matter (PM), unburned hydrocarbons, CO and aldehydes [15]. Due to their branched alkyl substituents, they can also be considered as "octane

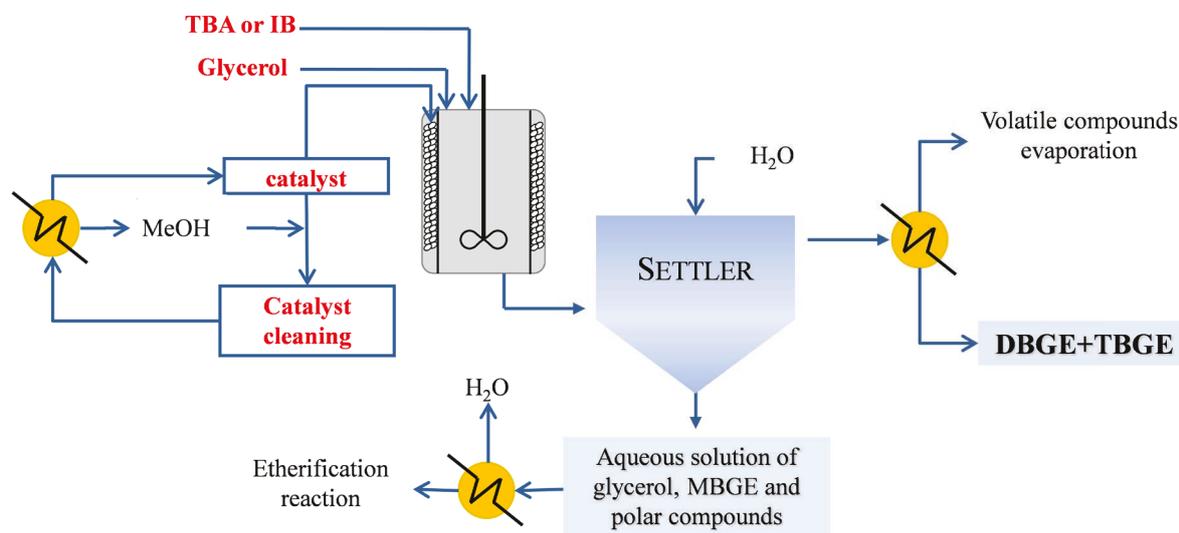* E-mail: francesco.frusteri@itae.cnr.it

Figure 1. Scheme of glycerol etherification reaction in presence of IB or TBA and GTBE purification.

boosters" for gasoline, thus representing a valid alternative to tertiary alkylethers (MTBE and ETBE) normally used as commercial gasoline additives [14].

Tert-butylation of glycerol may be carried out by using an *O*-alkylation agent such as isobutylene (IB), *tert*-butyl alcohol (TBA) or a C_4-fraction obtained from pyrolysis, fluid catalytic cracking or dehydrogenation processes of C_4 hydrocarbons. In particular, glycerol *tert*-butyl ethers (GTBE) can be obtained in three consecutive reversible reactions resulting in a mixture of five different glycerol ethers: two *mono-tert*-butylglycerol ethers (1-MBGE and 2-MBGE), two *di-tert*-butylglycerol ethers (1,3-DBGE and 1,2-DBGE) and one *tri-tert*-butylglycerol ether (TBGE). Since the *mono*-ethers of glycerol are more polar than *di*- and *tri*-ethers and have low solubility in diesel fuel and therefore cannot be used as fuel additives, the reaction of etherification must be directed towards the formation of more soluble *poly*-substituted ethers [16]. As depicted in Fig. 1, if the glycerol ethers mixture contains a large amount of *mono*-ethers some extra steps must be added in order to separate MBGEs from DBGEs and TBGE, which will increase in the overall cost of the process.

In the last decade several papers have been published describing the use of solid acid catalysts to produce *poly*-substituted ethers from glycerol, mainly in the presence of isobutylene (IB) as a reactant [14,17-23]. Generally, the resistance to catalyst deactivation and the formation of side products present the main problems. Additionally, when *tert*-butyl-alcohol (TBA) is used as a reactant [24-29], the water formed during the reaction prevents, due to equilibrium

restrictions, the synthesis of *poly*-substituted ethers, which is a significant limitation of this method.

In this paper the attention has been focused on exploring the feasibility of an efficient process of producing oxygenated additives, based on the glycerol etherification reaction, by using different reactants and acid solid catalysts, based on perfluorosulphonic ionomers. The use of a water permselective membrane is proposed to overcome the problem arising from the formation of water in case TBA is used as reactant.

2. Experimental procedure

Solid acid supported catalysts were prepared by incipient wetness method by using two spherical silica samples: (PQ Corporation) ES70Y and MS3030. An ethanolic solution containing about 17wt.% of Hyflon® Ion S4X perfluorosulphonic ionomers with equivalent weight (EW) of 730 was used as acid precursor. The EW corresponds to the concentration of sulphonic acid groups in each equivalent unity [17]. A-15 (dry) acid ion-exchange catalyst was used as a reference catalyst. Anhydrous glycerol and *tert*-butyl alcohol (TBA), supplied by Sigma Aldrich, and isobutylene (IB) 3.0, supplied by PQ Corporation, were used as reactants.

Surface area (SA_{BET}) and pore volume (PV) values of catalysts were determined from the nitrogen adsorption/desorption isotherms at 77 K using a Carlo Erba (*Sorptomatic Instrument*) gas adsorption device. The active phase loading and the thermal stability of H730/ES70Y and H730/MS3030 catalyst were evaluated by thermo-gravimetric and differential calorimetric

analysis, whereas the acid properties were evaluated by potentiometric titration as described elsewhere [17].

The etherification reaction was carried out in the presence of either isobutylene or *tert*-butanol in a 300 cm^3 stainless steel batch reactor under a stirring frequency of 1200 min^{-1}. IB was added in a liquid state and pushed into the reactor by nitrogen carrier flow at 5 bar. Experiments were performed at different reaction times (6-17 h), at a IB/GLY molar ratio ($R_{IB/GLY}$) ranging from 2.5 to 4 and using a catalyst amount of 3.0-7.5 wt.%, with respect to the glycerol weight ($R_{cat/GLY}$), 16-25 mesh in size. When using TBA, the pressure was autogeneous and the $R_{TBA/GLY}$ was 4 mol mol^{-1}.

When using TBA, in order to continuously remove the water formed during the reaction, a tubular membrane coupled with the batch reactor was used. Specifically, the gas phase (containing TBA, H$_2$O and the products) was recirculated through an HybSi membrane, furnished by Pervatech BV, maintained at the same temperature as the reaction. A vacuum of approximately 10 mbar was ensured at the permeate side of the membrane to avoid the condensation of water. The recirculation of gas stream was maintained constant by using a gas-pump equipped with a variable potentiometer. At the end of the experiments the reactor was cooled down in an ice-bath until the vapour pressure of the mixture decreased to the atmospheric pressure, thus allowing all the gas phase compounds to condense.

The liquid reaction mixture was analyzed *off*line by using a gas chromatograph HP 6890N equipped with a capillary column HP Innowax (l, 30 m; i.d., 0.53 mm; film thickness, 1.0 μm) and an automatic sampler.

The liquid phase was analyzed by GC-MS Agilent 5975C equipped with a capillary column DB-Waxter (l, 30 m; i.d., 0.25 mm; film thickness, 0.25 μm). The commercial solutions of *mono-tert*-butylethers (MBGEs) compounds and 2,4,4-trimethyl-1-pentene, representative of the *di*-isobutylene family of compounds, were used as standard references for the GC analysis while the response factors of *di*- and *tri*-ethers were deduced.

3. Results and discussion

## 3.1 Etherification reaction in presence of isobutylene (IB)

Isobutylene represents the main *O*-alkylation agent employed in the etherification reaction. Usually glycerol etherification with IB occurs at a high rate, even if the fromation of the desired *poly*-substituted ethers strongly depends on the reaction conditions employed [14,17-20].

Etherification of glycerol with isobutene is normally performed in a liquid phase, but unfortunately, IB is not very soluble in glycerol and, at the beginning, before the reaction starts, the reactants separate into two liquid phases.

Normally, with IB, reaction occurs as follow:

GLY + IB ⇆ MBGEs   (1a)
MBGEs + IB ⇆ DBGEs   (2a)
DBGEs + IB ⇆ TBGE   (3a)

However, some side reactions can also occur as shown below:
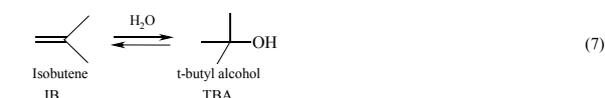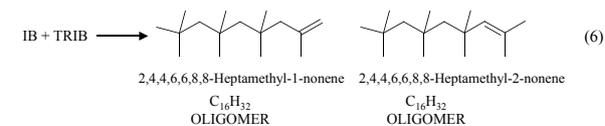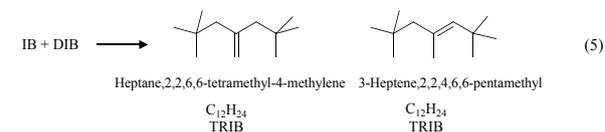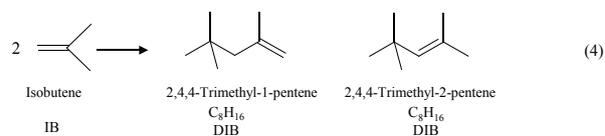
As already reported, the commercial strong acid ion exchange resins promote the oligomerization of isobutene (Reactions 4-6). In particular, in fact, Amberlyst 15 has also been used as a catalyst in either the isobutene dimerization [30] or in its trimerization. literature evidences show [31] that the surface of the sulphonated catalysts is the most active in dimerization of isobutene and that such reaction has been confirmed to be of a second order with respect to the amount of active acid sites.

So, by considering the importance of both the surface and the textural properties [17], in the attempt to limit the oligomerization reaction and to promote the formation of a mixture containing a low amount of *mono*-ethers, a Hyflon®-based system has been developed with the purpose of combining the hydrophobic character of the ionomer with its acidic properties. The Hyflon® structural polymeric unit is depicted in Fig. 2.

The main physico-chemical properties of the catalysts prepared and tested in the glycerol etherification with IB and with TBA are reported in Table 1.

notwithstanding the Hyflon-spherical silica catalysts are characterized by high SA$_{BET}$, their acidity is rather low (0.14-0.17 meqH$^+$/g$_{cat}$) if compared with the Amberlyst catalyst: this is likely due to the fact the acidity of

**Table 1.** Main physic-chemical properties of catalysts employed in the glycerol etherification.

Catalyst	Active Phase loading (wt.%)	SA_{BET} (m^2g^{-1})	PV (cm^3g^{-1})	APD (Å)	Acidity ($meqH^+g_{cat}^{-1}$)	Acidity ($meqH^+g_{ion}^{-1}$)
H-730/MS3030	18.12	177	0.33	77	0.14	0.77
H-730/ES70Y	19.14	204	0.33	118	0.17	0.88
A-15	-	45	0.40	355	4.50	4.50

SA= Surface Area and PV=Pore Volume, determined from the nitrogen adsorption/desorption isotherms at 77 K. APD=Average Pore Diameter.

Table 2. Glycerol etherification reaction in presence of IB.

Catalyst	X_{GLY} (%)	Product Distribution (wt.%)*					Y_{D+T} (%)	Ref.
		DIB	MBGEs	DBGEs	TBGE	Extra		
H730/ES70Y	41.0	1.0	57.9	39.2	1.9	-	13.9	[17]
H730/ES70Y powder	56.8	3.3	49.8	41.2	2.7	3.0	19.1	
A-15	30.0	4.0	72.3	18.3	3.6	1.8	5.3	[17]
A-15 powder	96.2	3.0	17.0	58.8	20.8	0.4	73.3	

$R_{IB/GLY}$ 2.5 mol mol^{-1}; $R_{cat/GLY}$ 3 wt.%; T_R, 70°C, 6 h.
*Selectivity normalized by excluding the IB amount
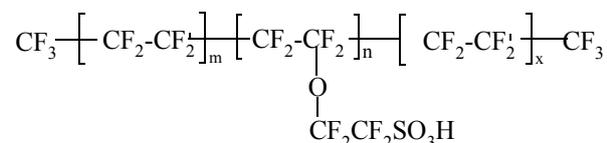
Figure 2. Hyflon® structural polymeric unit.

bulk monomer is about 1.2 meqH+/g_{ion} (three times lower than that of A-15) and that the Hyflon catalyst loading is about 17 wt%.

From the catalytic results reported in Table 2, it can be seen that, under the same reaction conditions, a great enhancement catalytic activity was obtained by using A-15 in powdered form, which allowed obtaining an almost total glycerol conversion (96.2%) and a yield of *poly*-ethers of 73.3%.

This result can be associated with the internal diffusion constraints within the cross-linked matrix of the A-15 resin, which causes a "lag" period when the catalyst is used in a beads form. Then, as the reaction goes on, the accumulated MBGEs (Reaction 1a) act as a solvent for both glycerol and IB thus facilitating the transport of the reactants within the pores, which results in an increase of the reaction rate. By using the powdered A-15, the internal diffusion control becomes negligible and the complete conversion of glycerol can occur within a shorter time [19]. On the contrary, in regards to the H730/ES70Y catalyst, the use of the powder sample, instead of a 16-25 mesh, only partially improves the glycerol conversion (56.8%) with a consequent increase in the *poly*-ethers yield to 19.1%. This result clearly shows the key role of the catalyst

particle size in the reactions carried out in the liquid phase.

In order to check how the reaction time may affect the progress of the reaction, the experiments have been carried out at different at different time (6 h and 17 h) and with different amount of the catalyst with different amounts of catalyst. From the results reported in Table 3 it can be seen that by increasing the amount of the catalyst and maintaining a non-stoichiometric IB/GLY molar ratio (2.5) the glycerol conversion, after 6 h, increased to 96.1% (compare run 1 with run 3) with an increase in *poly*-ethers yield from 5.3 to 67.0%. This result demonstrated an almost direct proportionality between the reaction rate and the catalyst loading.

By increasing the $R_{IB/GLY}$ molar ratio to 3 mol mol^{-1} (run 5) an almost total glycerol conversion was reached. Under such reaction conditions, the selectivity to MBGEs decreases to 16.1% thus attaining a *poly*-ether yield of 83.0%. From an overview of the results reported in Table 3 it is interesting to observe that, in all cases, an almost total glycerol conversion can be reached, but with different selectivity towards glycerol ethers. Specifically, under the first condition, the concentration of the *mono*-ethers still maintains very high (32.0%) with a proportional *poly*-ethers yield of 65.0%. While considering the second conditions, a longer reaction time allowed for further decrease in the *mono*-ethers selectivity, thus suggesting that the etherification reaction went on with an increase in the *poly*-ethers yield from 67.0 to 77.2%. At the end, by using a stoichiometric IB/GLY molar ratio and a high amount of catalyst (run 6), a long reaction time causes the decrease in the

Table 3. Influence of the reaction time in the etherification reaction by IB under different reaction conditions.

Run	Reaction time	X_{GLY} (%)	Selectivity					Y_{D+T} (%)
			1-MBGE	2-MBGE	1,3-DBGE	1,2DBGE	TBGE	
1	6 [a]	30.1	79.3	3.3	11.3	3.8	2.4	5.3
2	17 [a]	96.7	32.0	0.8	51.2	6.8	9.2	65.0
3	6 [b]	96.1	27.4	0.8	52.4	6.7	12.8	67.0
4	17 [b]	98.3	20.8	0.6	54.7	8.5	15.3	77.2
5	6 [c]	99.3	16.1	0.3	54.9	7.4	21.3	83.0
6	17 [c]	98.7	25.6	0.1	52.8	7.3	13.7	72.9

[a] Catalyst, A-15; $R_{IB/Gly}$ 2.5 mol mol^{-1}; $R_{cat/Gly}$ 3 wt.%; T_R, 70°C.
[b] Catalyst, A-15; $R_{IB/Gly}$ 2.5 mol mol^{-1}; $R_{cat/Gly}$ 7.5 wt.%; T_R, 70°C.
[c] Catalyst, A-15; $R_{IB/Gly}$ 3 mol mol^{-1}; $R_{cat/Gly}$ 7.5 wt.%; T_R, 70°C.

Table 4. Comparison of Hyflon-based catalysts with commercial A-15 resin in the glycerol etherification reaction by IB.

Catalyst	X_{GLY} (%)	Product Distribution (wt.%)*					Y_{D+T} (%)
		DIB	MBGEs	DBGEs	TBGE	Extra	
H730/MS3030	98.6	0.9	12.6	60.5	25.8	0.2	81.1
H730/ES70Y	99.1	1.1	12.4	60.3	25.6	0.6	81.7
A-15	98.7	10.2	16.9	54.8	15.9	2.2	72.9

$R_{IB/Gly}$ 3 mol mol^{-1}; $R_{cat/Gly}$ 7.5 wt.%; T_R, 70°C, 17 h.
*Selectivity normalized by excluding the IB amount.

poly-ethers yield with a correspondent increase in the mono-ethers concentration. This indicates that, once the equilibrium was reached, reaction no longer went on towards the formation of TBGE, rather the dealkylation of poly-ethers to mono-ethers was favored [17].

The results obtained by using the Hyflon®-based catalysts, after 17 h of reaction, are reported in Table 4. It can be seen that both two systems reached an almost total glycerol conversion and a yield of poly-ethers close to 81% (81.1-81.7%), higher than that obtained with the A-15 resin (~73%). Specifically, under such reaction conditions the Hyflon®-based catalysts allowed to obtain a TBGE concentration higher (25.6-25.8wt.%) than that obtained with the A-15 catalyst (15.9 wt.%).
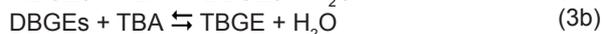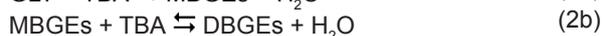
Moreover, it must be underlined that by using a Hyflon® based catalyst the IB oligomerization reaction (see reaction 4) takes place at a lower rate (DIB, 0.9-1.1%). This result could be explained by considering the lower acid sites density on the Hyflon® catalysts with respect to the A-15. Moreover, the hydrophobic or hydrophilic nature of the surface catalyst could also play a role in the oligomerization reaction, by affecting the IB surface retention. For example, the presence of fluorine atoms of Hyflon® could inhibit the adsorption of IB, whereas divinylbenzene matrix of A-15 may favor such adsorption promoting the DIB formation [25,31].

Overall, these results suggest that the etherification of glycerol with IB does not require the use of a catalyst characterized by a high number of acid sites, rather of a catalyst with adequate properties and most likely easily accessible acid sites.

3.2. Etherification reaction in presence of tert-butyl alcohol (TBA)

The use of TBA, which acts both as a reactant and a solvent, allows to overcome the technological problems arising from the management of the complex three-phases system which is the case when IB is used as O-alkylation agent.

Nevertheless, when TBA is used, water forms according to the following reaction scheme:

$$GLY + TBA \leftrightarrows MBGEs + H_2O \qquad (1b)$$
$$MBGEs + TBA \leftrightarrows DBGEs + H_2O \qquad (2b)$$
$$DBGEs + TBA \leftrightarrows TBGE + H_2O \qquad (3b)$$

Therefore, the reaction will be controlled by the equilibrium and the formation of poly-substituted ethers will depend on the water concentration in the liquid phase. In addition, water could also compete with the acid sites of the catalyst causing negative effects on reaction kinetics and catalyst deactivation.

The Hyflon® based catalysts have been tested in the glycerol etherification reaction with TBA and the results, obtained at 70°C after 6 h of reaction by employing

Table 5. Comparison of Hyflon-based catalysts with commercial A-15 resin in the glycerol etherification reaction with TBA.

Catalyst	X_{GLY} (%)	Product distribution (wt. %)					Y_{D+T} (%)
		DIB	MBGEs	DBGEs	TBGE	Extra	
H730/MS3030[a]	12.1	0.2	83.6	5.1	0.0	11.1	0.5
H730/ES70Y [a]	13.3	0.3	77.0	9.3	1.8	11.6	1.2
A-15 [a]	74.5	0.2	72.9	14.7	0.0	12.2	9.5
A-15[b]	78.9	0.4	56.2	30.0	0.8	12.6	22.3

[a] $R_{TBA/Gly}$, 4 mol mol^{-1} ; $R_{cat/Gly}$ 3 wt.%; T_{R}, 70°C; t, 6 h.
[b] $R_{TBA/Gly}$, 4 mol mol^{-1} ; $R_{cat/Gly}$ 7.5 wt.%; T_{R}, 70°C; t, 6 h.
*Selectivity normalized by excluding the TBA amount.

Table 6. Etherification reaction with TBA with commercial A-15 resin with and without the use of the permselective membrane.

X_{GLY}	Product distribution (wt. %)							Y_{D+T}
	DIB	TBA	MBGEs	DBGEs	TBGE	GLY	Extra	
84.0	0.9	58.0	17.7	12.8	0.8	3.2	6.6	29.9
93.5[a]	17.0	1.9	26.9	42.8	7.6	2.7	1.1	53.2

$R_{TBA/Gly}$, 8 mol mol^{-1} ; $R_{cat/Gly}$ 7.5 wt.%; T_{R}, 80°C; t, 27 h.
[a] Reaction in presence of the permselective membrane.

3wt.% of catalyst in respect to the glycerol weight, are reported in Table 5, compared with activity of the commercial A-15 resin. The best activity is shown by the A-15 resin, when the glycerol conversion attains a value of 74.5%, although the yields to poly-substituted ethers is very low, about 10%. The Hyflon®-based catalysts showed to be less active than A-15, with a glycerol conversion under 15%.

By using a larger amount of a catalyst (7.5 wt.%), in the presence of A-15, the glycerol conversion increases to 79%, but a Y_{D+T} of 22.3% is still very low if compared to the results obtained with IB.

By considering that a higher TBA/GLY molar ratio, a higher $R_{cat/gly}$ and that a temperature of 80°C could favor the etherification reaction in the presence of TBA [17,25], an experiment was carried out using the A-15 catalyst for a long reaction time (27 h). The results are reported in Table 6. It is possible to observe that that, notwithstanding the long reaction time, the yield of poly-substituted ethers does not exceed 30%, with a glycerol conversion of 84.0%, just to confirm that the thermodynamic constraints limit the total glycerol conversion and the glycerol ethers production.

Therefore, the water formed during the reaction inhibits the glycerol etherification reaction and, independently from the catalyst employed, its removal from the reaction medium is necessary to promote the formation of di- and tri-ethers.

So, in an attempt to remove the water produced during the reaction and thus to overcome the equilibrium restrictions, an experiment using a tubular membrane, normally employed to separate water from alcohols, coupled with the reactor, was carried out. To be specific, the gas phase, containing both the unconverted TBA and the products, passed through a membrane for selective and continuous water removal. The result obtained is reported in Table 6 too. Further, in addition to an increase in glycerol conversion (from 84.0 to 93.5%) the yield of poly-ethers drastically increased from 29.9 to 53.2%, thus highlighting the benefit obtained by using the membrane. Unfortunately, at the same time a large amount of di-isobutylene (DIB, 17%) was formed, very probably because of a high rate of dehydration of TBA to IB favored by a selective water permeation.

However, this preliminary result clearly indicates that the equilibrium can be shifted towards poly-ethers by using a membrane, but at the same time the design of a suitable catalyst and the optimization of the reaction conditions are necessary to limit the formation of the side products, such as DIB.

4. Conclusions

The performance of the two investigated systems was compared and the results reported here reveal that when using IB as a reactant, the glycerol etherification reaction proceeds with a high rate regardless of the catalyst employed. However, with Amberlyst characterized by a high acidity, the formation of the undesired products, such as DIB, presents a serious problem. When TBA is used as a reactant, in addition to observing a decrease in the reaction rate the formation of poly-ethers is hindered by formation of water causing

some thermodynamic restrictions. With TBA, even in the presence of a strong acid catalyst like Amberlyst, the yield of *poly*-ethers never exceeds 30%, proving that the water removal from the reaction medium is absolutely necessary. Based on these results, a first attempt to use a water permselective membrane coupled with the batch reactor provides encouraging results. Both the conversion of glycerol and the yield of *poly*-ethers increase significantly. In particular, in the presence of the membrane the conversion of glycerol reaches values close to 94% and the yield of *di*- and *tri*- ethers doubles.

Acknowledgements

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