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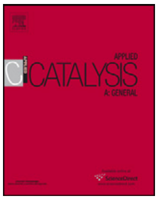

Synthesis of ethyl octyl ether from diethyl carbonate and 1-octanol over solid catalysts. A screening study

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ABSTRACT

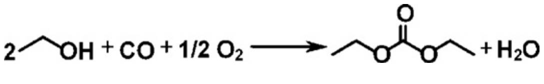
The synthesis of ethyl octyl ether (EOE) from a mixture of diethyl carbonate (DEC) and 1-octanol (1:2 molar ratio) over several solid catalysts was studied in batch mode at 150 °C and 25 bar. Catalyst screening revealed that EOE could be successfully obtained over some acid catalysts. In particular the highest yield was achieved over acid ion-exchange resins (33% after 8 h). A reaction scheme of the process is proposed. Selectivity to EOE was mainly affected by the production of diethyl ether (DEE) and di-n-octyl ether (DNOE). However, EOE was the main ether obtained (60 mol%), followed by DEE (20 mol%) and DNOE (20 mol%). By comparing the behavior of several acid resins, it was seen that the synthesis of EOE was highly related to the structural resin properties. It was found that the accessibility of DEC and 1-octanol to acid centers was improved over highly swollen and low polymer density resins. Thus, gel-type resins with low divinylbenzene content are the most suitable to produce EOE (e.g., Amberlyst 121, Dowex® 50Wx2-100 and CT224).

1. Introduction

In order to reduce the environmental impact of diesel exhaust emissions (particulate matter, unburned hydrocarbons, CO and NO_x), it is mandatory to improve the burning quality of diesel fuels [1,2]. The ideal diesel fuel for accomplishing this aim should be composed by linear paraffins with 10–20 carbon atoms, high cetane number and proper cold flow properties [3]. As a result, oil industry addresses its efforts to increase the yield in diesel cuts of refinery processes and thus commercialize better diesel fuel blends. A complementary strategy could be reformulating diesel fuels by including linear ethers [4–7]. Ethyl octyl ether (EOE) is an interesting candidate to be used in blends with commercial gasoil because of its properties: 10% oxygen content (w/w), 187 °C boiling point, d_4^{20} of 0.771, cetane number of 97 and satisfactory lubricity [8].

Industrially, it has been claimed that linear long chain ethers combined with peroxides as supplements to diesel fuels provide an environmental reduction of air pollutants. An amount of ethers about 1–5% (v/v) increased the cetane number from 2 to 20 points [1]. These ethers can be prepared by the traditional Williamson method from an alkoxide and alkyl halide [9]. However, dialkyl ethers are readily produced by acid catalyzed dehydration of alcohols more efficiently [10–12].

A green alkylation route to produce asymmetrical ethers is achieved with carbonates. Dimethyl carbonate has been proposed as methylating agent of several substances and reacts either as a methoxycarbonylating or as a methylating agent depending on the operation conditions [13]. In particular, the octanol alkylation from dimethyl carbonate clearly showed to be more efficient than using directly methanol [14]. As dimethyl carbonate, diethyl carbonate (DEC) is generally accepted as an environmentally benign ethylating agent [15–19]. An advantage of using DEC is that it can be obtained from ethanol (Eq. (1)). As a consequence, EOE would be a synthetic bio-fuel and could get the proper tax reduction, compensating partially their production costs higher than current commercial diesel.



(1)

A drawback to use alkyl carbonates is that their decomposition generates CO_2 as a by-product. However, the formation of carbonates from CO_2 is an interesting way for recycling it to fuels. Several advances in this direction have been reported and cyclic carbonate synthesis is already been industrialized [20–22]. Focused on linear carbonates, CO_2 reacts with alcohols in the presence of metal complexes (Eq. (2)). Due to the problems with the hydrolysis of the carbonate, 3 Å molecular sieves were used as drying agents to extract out the formed water. By using a dehydrative agent, an

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Nomenclature

DEC	diethyl carbonate
DEE	diethyl ether
DNOE	di-n-octyl ether
DOC	dioctyl carbonate
d_p	particle diameter (mm)
DVB	divinylbenzene
EOC	ethyl octyl carbonate
EOE	ethyl octyl ether
EtOH	ethanol
G	gel-type resin
$[H^+]$	acid capacity (meq/g)
$[H^+]/V_{sp}$	acid centers per volume unit in a swollen polymer state (meq H^+/cm^3)
ISEC	inverse steric exclusion chromatography
M	macroreticular resin
OcOH	1-octanol
$[OH^-]$	basic capacity (meq/g)
$R_{DEC/1\text{-}octanol}$	DEC to 1-octanol initial molar ratio (mol/mol)
S_{BET}	BET surface area in dry state (m^2/g)
S_{DEC}^{EOE}	selectivity to EOE with respect to DEC (%, mol/mol)
T	temperature (°C)
T_{max}	maximum operating temperature (°C)
V_{sp}	volume of the swollen polymer phase (cm^3/g)
W	mass of dry catalyst (g)
X_{DEC}	DEC conversion (%, mol/mol)
Y_{DEC}^{EOE}	yield to EOE with respect to DEC (%, mol/mol)

interesting dimethyl carbonate yield was achieved (55% based on MeOH) and byproducts were not significantly produced [23].

$$2\,R\text{-}OH + CO_2 \rightleftharpoons R\text{-}O\text{-}C(=O)\text{-}O\text{-}R + H_2O \quad (2)$$

Recently, EOE was synthesized successfully from ethanol and 1-octanol over acid gel-type resins at mild conditions ($T = 150\,°C$, $P = 20$ bar) [24]. In addition to EOE, diethyl ether (DEE) and di-n-octyl ether (DNOE) were detected as by-products. The differences between these ethers as diesel components are significant: DNOE has excellent properties to be blended with commercial diesel, whereas the high volatility of DEE is a serious drawback for its addition in large quantities to the diesel pool. Because acid resins easily catalyze the synthesis of short chain ethers, ethanol is preferred to be the limiting reactant in order to reduce DEE formation and to increase EOE production.

The present paper is devoted to study the liquid phase synthesis of EOE from DEC and 1-octanol over solid catalysts. A catalyst screening is carried out in order to select suitable catalysts for obtaining EOE. Moreover, the effect of the catalyst structure is related to DEC conversion and EOE yield.

2. Experimental

2.1. Materials

1-Octanol (≥99.5%, Fluka) and DEC (≥98%, Fluka) were used as reactants. Distilled water, ethanol (≥99.8%, Panreac), DEE (≥99%, Panreac), 1-octene (≥97%, Fluka) and DNOE (≥97%, Fluka) were used for analysis purposes. EOE was obtained and purified by rectification to 99% (w/w) in our lab.

Tested catalyst were supplied by Rohm and Haas (Amberlyst 26 OH, Amberlyst 21, Amberlyst 15, Amberlyst 35, Amberlyst 48, Amberlyst 46, Amberlyst 16, Amberlyst 36, Amberlyst 39, Amberlyst 70 and Amberlyst 121), Purolite (CT124 and CT224), Sigma (Dowex 50Wx8-100, Dowex 50Wx2-100, Nafion® NR 50, acid γ-Al_2O_3, basic γ-Al_2O_3) and Südchemie (H-BEA-25).

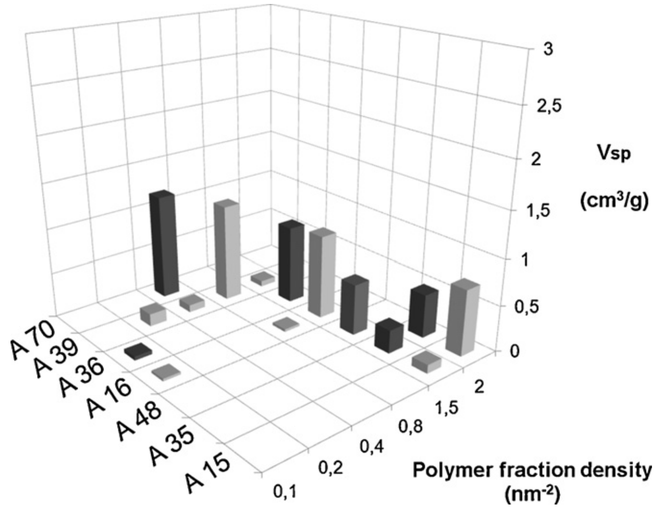

Fig. 1. ISEC pattern for used macroreticular resins.

A wide range of styrene-DVB resins were selected. In particular, a weak and a strong basic resins used in industrial processing were tested to check the behavior of basic catalysts (Table 1) [25]. Besides basic resins, 14 acid resins with different structural properties were tested (Table 2). Resins with low divinylbenzene (DVB) content are less crosslinked, and as a consequence with a more flexible structure. In the present work, the polarity of the reaction medium was high since 1-octanol was the main reactant and ethanol and water were obtained in significant amounts. Since ion-exchange resins swell in polar media, their morphology changes in the course of the reaction and non-permanent pores appear. A useful description of nature and characteristics of these pores in aqueous phase can be obtained from inverse steric exclusion chromatography (ISEC) data [12,26,27]. In macroreticular structures a part of new open spaces in the range of mesopores can be characterized by the cylindrical pore model. However, this model is not applicable to describe spaces between polymer chains formed as a result of polymer swelling. A good view of the three-dimensional network of swollen polymer is given by the geometrical model developed by Ogston [28], in which micropores are described by spaces between randomly oriented rigid rods. The characteristic parameter of this model is the specific volume of the swollen polymer (volume of the free space plus that occupied by the skeleton), V_{sp}. The Ogston model also allows to distinguish zones of swollen gel phase of different density or polymer chain concentration (total rod length per volume unit of swollen polymer, nm^{-2}) [26,29,30].

Distribution of the different polymer density zones of the swollen resins in water is shown in Figs. 1 (macroreticular) and 2 (gel-type). As seen, when the DVB resin content is high the polymer density is accordingly high, and V_{sp} values small. For instance, high crosslinked macroreticular resins such as Amberlyst 15 have a very high polymer density (1.5–2 nm^{-2}) and V_{sp} of about 0.8 cm^3/g, being as a result poorly accessible polymer. On the contrary, a very low-crosslinked gel resin such as Amberlyst 121 has much more space between chains (density: 0.2–0.8 nm^{-2}) and V_{sp} is about 3.3 cm^3/g. The pore distribution of the swollen gel phase in water is probably quite representative of the morphology of the catalyst in the reaction medium because the resin swelling in alcohols and water is comparable [12,26]. Thus, active centers in swollen state of low crosslinked gel-type resins are by far more accessible, and as a consequence the number of acid centers that could take part in the reaction is far higher.

Table 1
Properties of tested basic resins.

Catalyst	Short name	Basic strength	Type[b]	Basicity (meq OH^-/g)	S_{BET}[a] (m^2/g)	d_p (mm)	T_{max} (°C)
Amberlyst 21	A 21	Weak	M	4.6	25	0.58	100
Amberlyst 26 OH	A 26	Strong	M	2–2.6 [43,44]	30	0.63	60

[a] BET surface area in dry state (N_2 for $S_{BET} \geq 1$ m^2/g).
[b] M = macroreticular.

Table 2
Properties and structural parameters of tested acid resins.

Catalyst	Short name	Type[b]	DVB %	Acidity (meq H^+/g)	V_{sp} (cm^3/g)	S_{BET}[a] (m^2/g)	d_p (mm)	T_{max} (°C)
Amberlyst 15	A 15	M	20	4.81	0.823	42.01	0.65	120
Amberlyst 35	A 35	M	20	4.8	0.736	28.9	0.66	150
Amberlyst 48	A 48	M	High	5.62	0.563	33.8		
Amberlyst 46[c]	A 46	M	High	0.43	0.16	57.4	0.78	120
Amberlyst 16	A 16	M	12 [45]	4.8	1.245	1.69	0.56	130
Amberlyst 36	A 36	M	12 [46]	5.4	0.999	21.0	0.57	150
Amberlyst 39	A 39	M	8 [46]	5.0	1.451	0.09	0.54	130
Amberlyst 70[d]	A 70	M	8	3.01	1.189	0.02	0.55	190
Nafion NR-50	Nafion 50	G		0.89		0.35	2.40	180
Amberlyst 121	A 121	G	2 [47]	4.8	3.263	0.02	0.44	130
Dowex 50Wx8-100	Dow 8	G	8	4.83	1.627	0.23	0.17	150
Dowex 50Wx2-100	Dow 2	G	2	4.83	2.655	1.32	0.25	150
CT124	CT124	G	4	5.0	1.994	0.07	0.76	
CT224	CT224	G	4	5.34	1.811	0.945	0.33	150

[a] BET surface area in dry state (N_2 for $S_{BET} \geq 1$ m^2/g; Kr for $S_{BET} < 1$ m^2/g) – Accusorb ASAP 2020, Micromeritics-, samples were dried at vacuum.
[b] M = macroreticular; G = gel-type.
[c] Sulfonated only at the polymer surface.
[d] Chlorine substituting hydrogen atoms in polymer chains.

On the other hand, tested resins shows a wide range of acid capacities. Conventional sulfonated resins (e.g., Amberlyst 15) have a concentration of about a sulfonic group per styrene ring, statistically as para-substitution [31,32]. Over-sulfonated resins (e.g., Amberlyst 35) have a higher concentration of sulfonic groups because they have in some styrene rings more than one sulfonic group. The additional sulfonic groups are predominantly distributed close to the particle surface [33]. Amberlyst 46 is a resin sulfonated only at the polymer surface. It has all their acid sites accessible but its acid capacity is about a tenth of the other. Amberlyst 70 should be highlighted. It has chlorine atoms in its structure, which confer this catalyst a higher thermal stability, but its acid capacity is only about 3 meq H^+/g. Finally, NR50 (a gel-type copolymer of Teflon® and perfluoro-alkanesulfonic monomers) was also tested. Fluorine atoms of polymer chains upgrade thermal stability of NR50 and give a higher acid strength than PS-DVB resins.

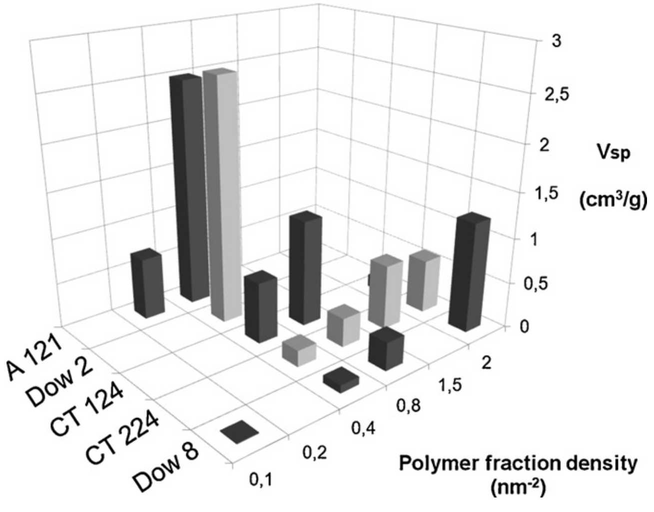

Fig. 2. ISEC pattern for used gel-type resins.

In addition to ion exchange resins, a zeolite and two aluminas (γ-Al_2O_3) were tested (Table 3). Both aluminas were supplied as activated form. Textural characteristics were derived from N_2 adsorption–desorption isotherms recorded at 77 K with an Accusorb ASAP 2020 sorptometer from Micromeritics (Norcross, G.A.), after outgassing the samples for 4 h at 500 °C. The SiO_2/Al_2O_3 molar ratio of H-BEA-25 was measured by X-ray fluorescence (PW1400, Philips; detector: LiF crystal; excitation source: Rh). Finally, skeletal density was measured by He displacement in an Accupyc 1330 (Micromeritics).

2.2. *Synthesis*

2.2.1. *Apparatus and analysis*

Experiments were carried out in a 100 mL-stainless steel autoclave operated in batch mode. Temperature was controlled by an electrical furnace. One of the outlets of the reactor was connected directly to a liquid sampling valve, which injected 0.1 μL of pressurized liquid into a gas–liquid chromatograph. The liquid composition was analyzed hourly by using a split mode operation in a HP6890A GLC apparatus equipped with a TCD detector. A 50 m × 0.2 mm × 0.5 μm methyl silicone capillary column was used to separate and determine reactants and products. The column was temperature programmed to start at 50 °C with a 10 °C/min ramp to reach 250 °C and held for 6 min. Helium (≥99.998%, Linde) was used as the carrier gas with a total flow rate of 30 mL/min. All the

Table 3
Properties of tested zeolite and aluminas.

	H-BEA-25	Acid γ-Al_2O_3	Basic γ-Al_2O_3
SiO_2/Al_2O_3	25		
Brönsted acid sites (meq H^+/g)	1.2	0.46	
Brönsted basic sites (meq OH^-/g)			0.57
S_{BET} (m^2/g)	503	151	139
Pore volume (cm^3/g)	0.663	0.255	0.265
Mean pore diameter (Å)	108	57	62
Skeletal density (g/cm^3)	2.237	3.281	3.327
d_p (mm)	0.0081	0.105	0.105

Table 4
Conversion and yield over some acid and basic catalysts at 6 h.

Type		Catalyst	X_{DEC} (%)	S_{DEC}^{EOE} (%)	Y_{DEC}^{EOE} (%)	T (°C)
Basic	Resin	A 26	10.2	–	–	100
		A 21	11.1	–	–	100
	Alumina	γ-Al_2O_3	7.4	2.5	0.2	150
Acid	Resin	CT224	91.8	34.0	31.2	150
		Nafion 50	59.7	31.4	18.8	150
	Zeolite	H-BEA-25	22.8	52.8	12.0	150
	Alumina	γ-Al_2O_3	6.2	3.5	0.2	150

$R_{DEC/1\text{-}octanol} = 0.5$, $W = 2$ g, 500 rpm.

species were identified by a second chromatograph equipped with a mass spectrometer (Agilent GC/MS 5973) and chemical database software.

2.2.2. *Procedure*

Amberlyst 21 was previously converted to OH^- form and both basic resins were first dried by methanol percolation [34], then in an oven at 80 °C for 3 h at atmospheric pressure and finally at 80 °C under vacuum overnight. Acid resins were dried at 110 °C for 3 h at atmospheric pressure and subsequently at 110 °C under vacuum overnight. The residual water content of dried resins was determined by a Karl Fisher titrator (Orion AF8). Analytical volumetric titrations showed <3% (w/w) of residual water in the tested resins, in agreement with reported data [35,36]. Otherwise, H-BEA-25 was activated at 500 °C and both aluminas were treated at 300 °C in an atmospheric oven; subsequently dried at 110 °C under vacuum overnight.

The reactor was loaded with 70 mL of DEC/1-octanol mixture (1:2 molar ratio), heated up to the desired temperature and stirred at 500 rpm. Pressure was set at 25 bar with N_2 to maintain the liquid phase. When the mixture reached the working temperature, 2 g of dried catalyst were injected into the reactor from an external cylinder by shifting with N_2. Resins were used with the commercial distribution of particles sizes, and zeolite and aluminas as a powder. Working conditions were selected since, as quoted in literature, liquid phase reactions of dehydration of 1-pentanol and 1-hexanol to linear ethers take place at these conditions in the same set-up free of external and internal mass transfer influences [10,37]. It is to be noted that molecular size of such alcohols and ethers is similar to that of DEC and EOE, respectively. Catalyst injection was taken as zero time. Temperature was set at 100 °C for basic resins (because of their low thermal stability) and 150 °C for all the other catalysts.

In each experiment, DEC conversion (X_{DEC}), selectivity to EOE (S_{DEC}^{EOE}) and yield to EOE with respect to DEC (Y_{DEC}^{EOE}) were estimated by Eqs. (3)–(5), respectively.

$$X_{DEC} = \frac{\text{mole of DEC reacted}}{\text{mole of DEC initially}} \times 100 \quad [\%, \text{mol/mol}] \tag{3}$$

$$S_{DEC}^{EOE} = \frac{\text{mole of DEC reacted to form EOE}}{\text{mole of DEC reacted}} \times 100 \quad [\%, \text{mol/mol}] \tag{4}$$

$$Y_{DEC}^{EOE} = \frac{\text{mole of DEC reacted to form EOE}}{\text{mole of DEC initially}} \times 100 = \frac{X_{DEC} \times S_{DEC}^{EOE}}{100} \quad [\%, \text{mol/mol}] \tag{5}$$

Experiments performed on Amberlyst 21, Amberlyst 26 OH, H-BEA-25, Amberlyst 15, Amberlyst 35, Amberlyst 48, Amberlyst 46, Amberlyst 70, CT224 and Dowex 50Wx2-100 were replicated three times to assure the reproducibility of the results. Thus, data shown in this study has a relative experimental error lower than 1.2% for X_{DEC}, 2.0% for S_{DEC}^{EOE} and 2.6% for Y_{DEC}^{EOE}, (95% confidence level) at 8 h of reaction time.

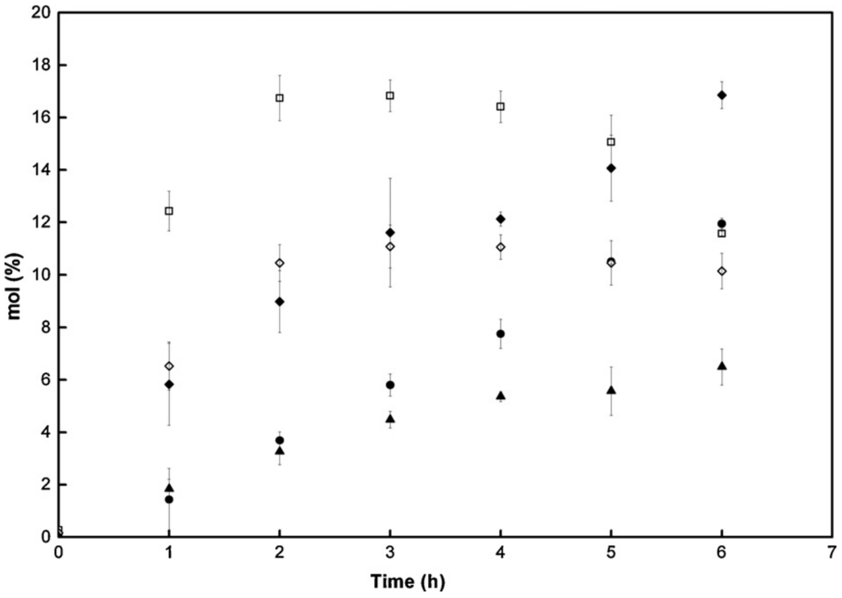

Fig. 3. Product distribution profile in liquid phase along time over CT224. $T = 150$ °C, $R_{DEC/1\text{-}octanol} = 0.5$, $W = 2$ g, 500 rpm. (□) Ethanol, (◇) EOC, (◆) EOE, (●) DEE, (▲) DNOE. The error bars indicate the confidence interval at a 95% probability level.

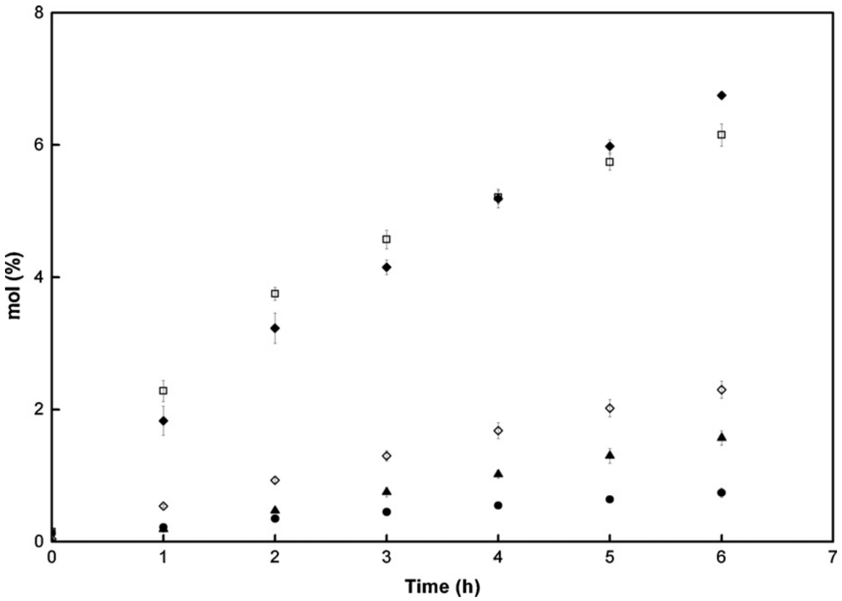

Fig. 4. Product distribution profile in liquid phase along time over H-BEA-25. $T = 150\,^{\circ}\mathrm{C}$, $R_{\mathrm{DEC/1\text{-}octanol}} = 0.5$, $W = 2\,\mathrm{g}$, 500 rpm. (□) Ethanol, (◊) EOC, (♦) EOE, (●) DEE, (▲) DNOE. The error bars indicate the confidence interval at a 95% probability level.

3. Results and discussion

3.1. Preliminary experiments

Blank experiments without catalyst were performed at 150 °C. The non-catalyzed reaction allowed only the carboxyethylation of 1-octanol to ethyl octyl carbonate (EOC) but in small amounts ($X_{\mathrm{DEC}} = 6\%$ at 6 h) and always $X_{\mathrm{DEC}} < 1\%$ at the initial time. In addition, it is seen that decomposition of carbonates (DEC and EOC) was not significant in the absence of catalyst. On the other hand, decomposition of DEC to DEE was checked over Amberlyst 121. Results state that the acid resin decomposes significantly DEC to DEE ($X_{\mathrm{DEC}} = 17\%$ at 6 h).

3.2. Catalyst screening

Table 4 summarizes the results of the catalyst screening runs. In general, the runs carried out over basic resins and both aluminas showed that DEC reactivity was low; therefore the EOE synthesis was not relevantly achieved. In the case of basic resins, the low conversions were probably due to the low working temperature. Unlike basic catalysts, DEC conversion is improved over acid catalysts. Specifically, the two types of catalysts that showed a relevant activity were acid resins and the zeolite, although at the working temperature the higher yields were achieved over acid resins. Similarly, zeolites were found to be less active catalyst to produce di-n-pentyl ether than acid ion-exchange resins [38]. Nevertheless, it is to be mentioned that zeolites have been reported as suitable catalyst to produce linear fuel ethers because they proved to be less sensitive to water inhibition, even at higher temperature [39].

On the other hand, it is observed in Table 4 that H-BEA-25 is less active but more selective to EOE than CT224. Figs. 3 and 4 show the liquid product distribution along time over CT224 and H-BEA-25. In addition to EOE, DNOE, DEE, ethanol and EOC, other by-products were detected in low amount (<3% molar): water, dioctyl carbonate (DOC), olefins and branched ethers, not shown for the sake of clarity. As seen, the product distribution profiles showed quite different trends along time. Over H-BEA-25, all products increased its molar percentage with time and EOC was low along the experiment. On the contrary, on CT224 a maximum in the concentration profile for ethanol and EOC was observed. As these products were consumed, the moles of EOE were increased steadily. It seems that on CT224 transesterification to EOC is faster than its decomposition to EOE. This trend is opposite to that observed on the zeolite where EOC is decomposed as it is formed. As expected selectivity to EOE rise steadily through the experiment.

The ethanol and EOC profiles suggest the reaction scheme of Fig. 5, in agreement with those reported in open literature to synthesize ethers from dimethyl carbonate [14,40]. EOE synthesis proceeds in two consecutive steps; the first (a) is the carboxylation of DEC to produce EOC and the second (b) the decomposition of EOC to EOE. The carboxylation step (a) would be kinetically favored over acid resins. However, reaction network is complex and the following side reactions take place in the reaction system:

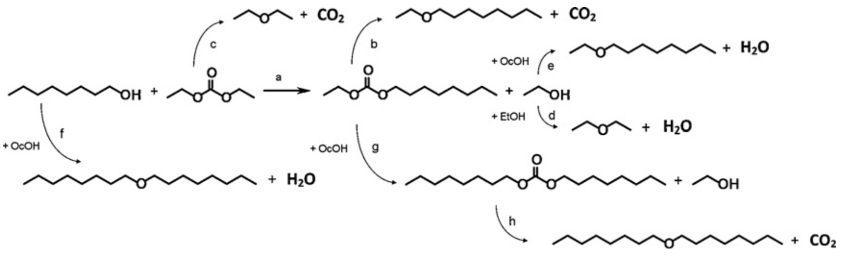

Fig. 5. Reaction scheme of EOE synthesis from DEC and 1-octanol.

Table 5
Ether average composition over Dowex 50Wx2 at 48 h.

Products	EOE	DEE	DNOE
% (mol/mol)	60.5	20.2	19.3
% (w/w)	60.8	9.5	29.6

T = 150 °C, $R_{\text{DEC/1-octanol}}$ = 0.5, W = 2 g, 500 rpm.

(1) DEC decomposition to DEE (c), which is undesired because of the extra consumption of diethyl carbonate.
(2) Carboxyocthylation of EOC (g) and subsequent decomposition to DNOE (h) as revealed by the presence of DOC as byproduct.
(3) Additionally to carbonate decomposition routes, linear ethers can be also produced from alcohols dehydration (d, e, f), because water was detected in the mixture as by-product.

Since the formed ethanol was partially dehydrated either with another ethanol (d) or with 1-octanol (e), it could be considered as an intermediate rather than a final product. As a result, the initial molar ratio (DEC/1-octanol) would be an important factor to hinder the dehydration of ethanol to DEE and, as a consequence, to increase the selectivity to EOE [24].

3.3. Acid resins

As the catalyst screening revealed that the highest EOE yield was achieved over acid styrene-DVB resins on a catalyst weight basis, 13 resins of different morphology and acid capacity were tested. The product distribution trends for all acid resin runs were similar to that shown in Fig. 3 and at 8 h almost all DEC was converted to ethylated products. However, there was still a significant amount of the intermediate products (EOC and ethanol), which should be able to produce more EOE. As a result, to study the potential of the system, a long time experiment was carried out on Dowex 50Wx2. It was seen that at 48 h all intermediates were consumed. Table 5 shows the final distribution of ethers: EOE was the main ether followed by DEE and DNOE, on a molar basis. Some octenes were also formed but ethene was no detected.

Table 6 shows DEC conversion, EOE selectivity and yield for tested acid styrene-DVB resins after 8 h. As a general rule gel type resins show a better behavior than macroreticular ones. It is also seen that in both gel-type and macroreticular resins EOE yield increases as the DVB% decreases, as a consequence of the higher DEC conversions and EOE selectivities observed. By comparing the macroreticular conventionally sulfonated resins Amberlyst 15, Amberlyst 16 and Amberlyst 39 resins with Amberlyst 46 it is seen that EOE yield on the last one is far smaller than on the other three resins, as expected because of the very low number of acid sites of Amberlyst 46. The low EOE yield is mainly due to the very low DEC conversion since EOE selectivity of Amberlyst 46 is only a bit lesser. Amberlyst 15 has only about a 5% of $-SO_3H$ groups placed at the polymer surface (≈0.25 meq H^+/g) [41]. Since this quantity is a half of the acid capacity of Amberlyst 46 (sulfonated only at the polymer surface) it can be inferred that in macroreticular resins other than Amberlyst 46 the reaction takes place essentially in the gel phase. Gel phase becomes active by the swelling of the polymer by permeation of alcohol and the retention of part of water released in the reaction.

Catalytic behavior of Amberlyst 15, Amberlyst 16 and Amberlyst 39 can be explained looking at the structure of the swollen gel phase. Gel phase density of swollen resins decrease in the order Amberlyst 15 (2 nm^{-2}; spaces between chains are equivalent to pores of less than 1 nm diameter [42]) > Amberlyst 16 (1.5 nm^{-2}; spaces are equivalent to pores of 1 nm diameter [42]) > Amberlyst 39 (0.8 nm^{-2}; spaces are equivalent to pores of 1.5 nm diameter [42]). The number of accessible sites to the reaction in Amberlyst 39 is higher, and spaces between polymer chains allow octanol and DEC to permeate and to accommodate better reaction intermediates. As a consequence, a higher DEC conversion and EOE selectivity is observed on Amberlyst 39. Similarly, Amberlyst 36 gives a better EOE yield than Amberlyst 35.

In the case of gel-type resins the higher EOE yield obtained on Amberlyst 121 and Dowex 50Wx2 are due to the fact that they show the higher V_{sp} values. In this way they are more swollen in the reaction medium and, in addition, with a polymer density of 0.4 nm^{-2} (equivalent to pores of 2.6 nm [42]) they give a better selectivity to EOE. Finally, by comparing data of Amberlyst 39 and Amberlyst 70, both resins conventionally sulfonated, it is seen that the latter shows a better EOE yield in spite of its acid capacity is about 60% of that of Amberlyst 39. Although they have similar swollen gel-phase volume, Amberlyst 70 has lower polymer density (0.4 nm^{-2} which is equivalent to pores of 2.6 nm diameter [42]) than Amberlyst 39.

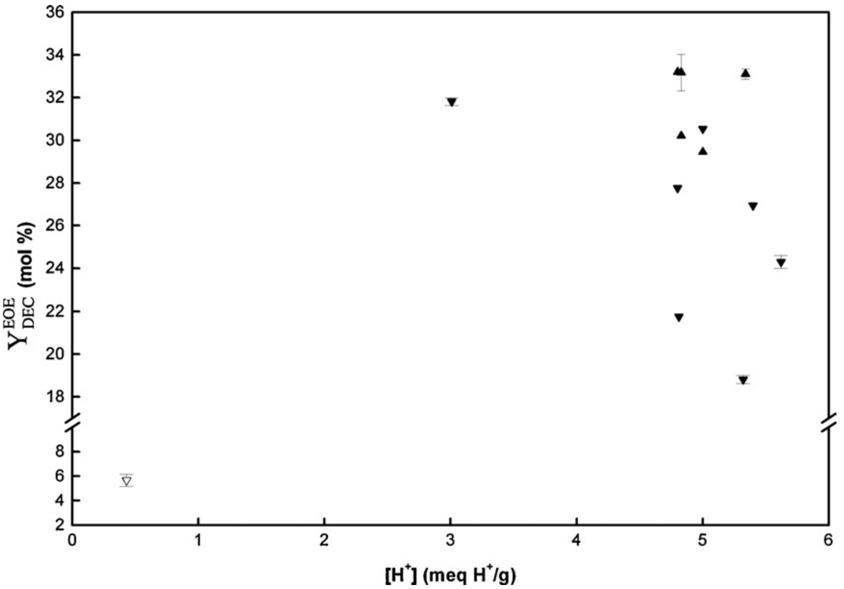

Fig. 6. Influence of resin acidity on yield to EOE with respect to DEC (Y_{DEC}^{EOE}) at 8 h. T = 150 °C, $R_{\text{DEC/1-octanol}}$ = 0.5, W = 2 g, 500 rpm. (▼) Macroreticular, (▲) gel-type, (▽) Amberlyst 46. The error bars indicate the confidence interval at a 95% probability level.

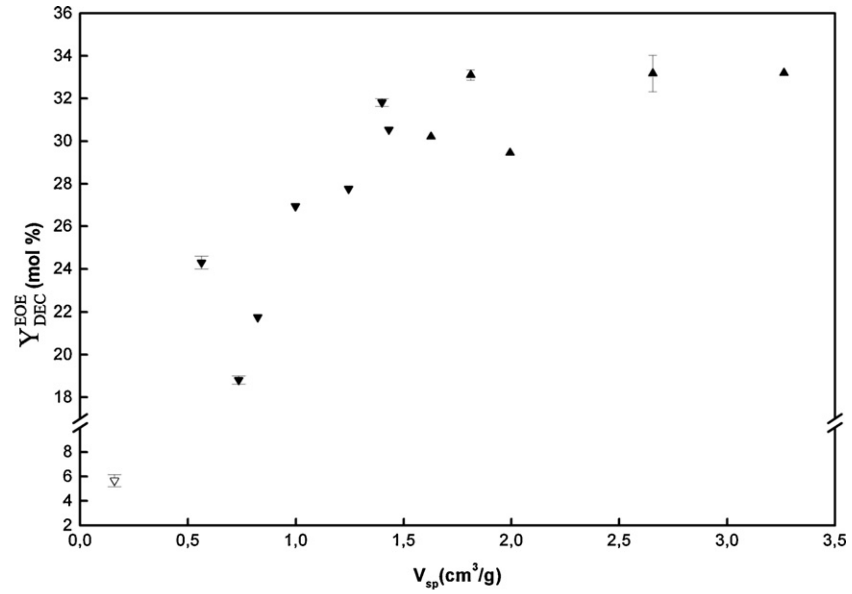

Fig. 7. Influence of swollen resin volume on yield to EOE with respect to DEC (Y_{DEC}^{EOE}) at 8 h. T = 150 °C, $R_{DEC/1\text{-octanol}}$ = 0.5, W = 2 g, 500 rpm. (▼) Macroreticular, (▲) gel-type, (▽) Amberlyst 46. The error bars indicate the confidence interval at a 95% probability level.

Again, the wider spaces between polymer chains favored the diffusion of 1-octanol and EOE as well as less steric restriction for the reaction intermediate.

However, the effect of the sulfonation degree is not clear because does not always upgrade the EOE yield (see Table 6). For instance, comparing among macroreticular resins with high percentage of DVB, Amberlyst 48/Amberlyst35/Amberlyst 15, it is seen that the best EOE yield is obtained on Amberlyst 48. It has the highest acid capacity of the three resins and shows the higher DEC conversion. In addition, despite of the fact that it is the least swollen of the three, EOE selectivity is something higher. Probably because the swollen gel phase in Amberlyst 48 has a smaller gel phase density (equivalent to 1 nm pores). EOE yield on Amberlyst 35 is worse than on Amberlyst 15 probably because the fraction of accessible acid sites is smaller in the former as pointed out by its lower V_{sp} value. Likewise, the pair Amberlyst 16/Amberlyst 36 (macroreticular, 12% DVB) shows better DEC conversion on Amberlyst 36 (in line with its higher acid capacity) but a higher EOE selectivity on Amberlyst 16 (in line with its higher V_{sp} value); in this case spaces between chains are almost equivalent). However, by comparing the pair CT124/CT224 (gel-type, 4% DVB) it is seen that the second has better DEC conversion (in line with the higher acid capacity) but it also shows a better EOE selectivity (despite its V_{sp} value is smaller, as well as the spaces between chains). It seems again that the effect of polymer swelling is more significant than the fact of having more acid centers if they are not accesible.

In order to state the influence of the resin structure on the catalytic behavior, the effect of acid capacity and structural parameters in swollen state on EOE yield was studied. Firstly, Fig. 6 plots the EOE yield versus the acid capacity. As shown, acid capacities of tested

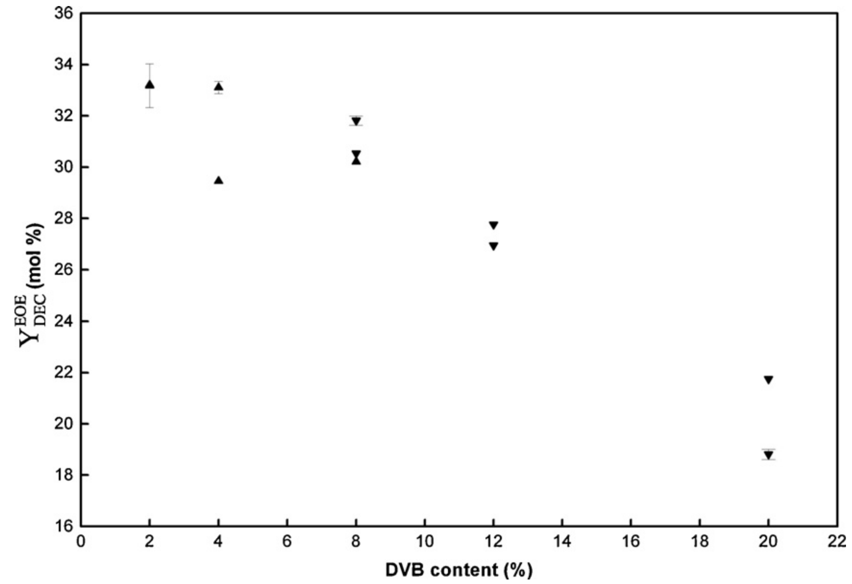

Fig. 8. Influence of DVB resin content on yield to EOE with respect to DEC (Y_{DEC}^{EOE}) at 8 h. T = 150 °C, $R_{DEC/1\text{-octanol}}$ = 0.5, W = 2 g, 500 rpm. (▼) Macroreticular, (▲) gel-type. The error bars indicate the confidence interval at a 95% probability level.

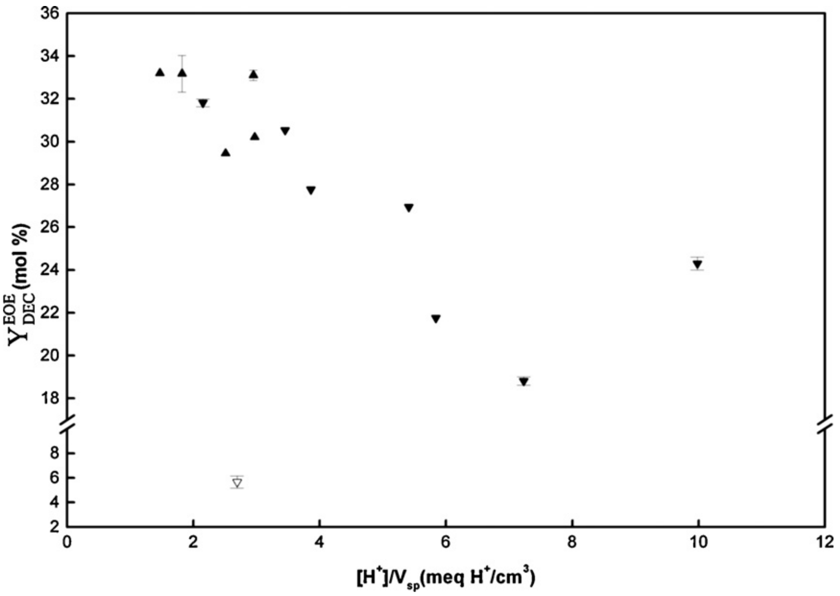

Fig. 9. Variation of the yield to EOE with respect to DEC (Y_{DEC}^{EOE}) vs. the acid centers per volume unit in a swollen polymer state (H^+/V_{sp}) at 8 h. $T = 150\,^{\circ}C$, $R_{DEC/1\text{-}octanol} = 0.5$, $W = 2$ g, 500 rpm. (▼) Macroreticular, (▲) gel-type, (▽) Amberlyst 46. The error bars indicate the confidence interval at a 95% probability level.

Table 6
$X_{DEC}/S_{DEC}^{EOE}/Y_{DEC}^{EOE}$ (%) at 8 h of acid resins related to their structure type, DVB content and sulfonation degree. $T = 150\,^{\circ}C$, $R_{DEC/1\text{-}octanol} = 0.5$, $W = 2$ g, 500 rpm.

Type	DVB (%)	Conventional Sulfonated	Over-sulfonated	Surface Sulfonated	Others
Macroreticular	High	79.3/27.4/21.8[a]	69.8/27.0/18.8[b] 83.7/29.03/24.3[c]	24.8/23.1/5.7[d]	
	12	85.4/32.5/27.8[e]	91.7/29.6/26.9[f]		
	8	93.6/32.6/30.5[g]			83.6/38.1/31.8[h]
Gel-type	8	90.9/33.2/30.2[i]			
	4	91.7/32.1/29.5[j]	95.0/34.9/33.1[k]		
	2	96.6/34.3/33.2[l] 95.8/34.6/33.2[m]			

[a]Amberlyst 15, [b]Amberlyst 35, [c]Amberlyst 48, [d]Amberlyst 46, [e]Amberlyst 16, [f]Amberlyst 36, [g]Amberlyst 39, [h]Amberlyst 70, [i]Dowex 50Wx8, [j]CT124, [k]CT224, [l]Dowex 50Wx2, [m]Amberlyst 121.

resins were similar (except for the particular resins Amberlyst 46 and Amberlyst 70) but they showed quite different activities in terms of EOE yield. It is also seen that gel-type resins gave higher yields than macroreticular ones at the same acid capacity, highlighting the significant role of the resin structure.

As mentioned above, V_{sp} (specific volume of swollen polymer) is a parameter that allows to know how much the resin swells in the reaction medium. Fig. 7 shows the positive effect of V_{sp} on Y_{DEC}^{EOE}. It is seen that measured EOE yield increases with V_{sp} until a plateau is reached for V_{sp} values of 2 cm^3/g. As shown in Figs. 1 and 2, both in macroreticular and in gel-type resins as V_{sp} increases density of polymer gel phase decreases. As a result, gel-phase is flexible enough and it could accommodate better the reaction intermediates, and the higher space between the polymer chains allows large molecules such as 1-octanol to access easier to a larger number of acid centers. Figs. 1 and 2 also show that resins with low DVB content have lower polymer fraction density in a polar medium and higher V_{sp}. Fig. 8 illustrates that Y_{DEC}^{EOE} increased on decreasing the DVB resin content. Accordingly, in order to obtain efficiently large molecules such as EOE, ion-exchange resins with V_{sp} of 2 cm^3/g or higher which correspond to resins with less than 8% of DVB are the most suitable. Between tested resins gel-type Amberlyst 121, CT-224 and Dowex 50Wx2-100 fulfill such requirements.

Finally, a parameter that estimates the concentration of acid centers per volume unit in swollen polymer state is the $[H^+]/V_{sp}$ ratio (meq H^+/cm^3). Fig. 9 shows the influence of $[H^+]/V_{sp}$ on the synthesis of EOE. It is seen that measured EOE yield decreases on increasing $[H^+]/V_{sp}$. It is to be noted that neither Amberlyst 46 (with all acid sites in the polymer surface) nor Amberlyst 48 (the resin with the highest acid capacity but also the less swollen one) follow the general trend. It can be concluded that the higher EOE yields are given by resins with low density of acid centers in the swollen polymer volume (less than 3 meq H^+/cm^3) and acid capacities of about 5 meq H^+/g or a bit higher. These requirements would be fulfilled by ion-exchange resins with high V_{sp} values and preferably conventionally sulfonated. Between tested resins, Dowex 50Wx2-100, Amberlyst 121 and CT224 show the higher EOE yields.

4. Conclusions

The catalyst screening revealed that EOE can be successfully produced in liquid phase from DEC and 1-octanol over acid catalysts at 150 °C. High DEC conversion and high EOE yield were achieved over acid resins.

A two-step pathway for EOE synthesis is proposed. Firstly, the transesterification of DEC to EOC takes place. Subsequently, EOC decomposes to EOE. Unfortunately, direct decomposition of DEC to DEE also occurs. Besides carbonate decomposition route, linear ethers are also produced from alcohols dehydration reactions.

On acid resins, after 8 h of reaction almost all DEC reacted to ethylated products. When the intermediates (EOC and ethanol) were consumed at 48 h, EOE was the main reaction product, followed by the two symmetrical ethers DEE and DNOE, on a molar basis.

The synthesis of EOE is highly related to structural resins properties. The accessibility of large molecules to acid centers is favored over resins with large space between polymer chains. Consequently, in order to synthesize large ethers such as EOE, a greatly expanded polymer network in swollen state is the most suitable resin property. It is also desirable that density of acid centers in the swollen resin would be low. These requirements can be found in low DVB content resins (e.g., gel-type resins as Dowex 50Wx2-100, Amberlyst 121 or CT224).

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