



Feature Article

Dehydration of 1-octanol to di-*n*-octyl ether in liquid phase with simultaneous water removal over ion exchange resins: Effect of working-state morphologies



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ABSTRACT

The influence of the concentration of polar reactants and products on the working-state morphology of ion exchange catalysts has been investigated over different acidic ion-exchange resins for di-*n*-octyl ether (DNOE) synthesis from 1-octanol dehydration at 423–448 K and atmospheric pressure in a batch reactor equipped with a Dean & Stark device. By removing water formed 1-octanol conversion was practically complete; the olefin formation being the main secondary reaction. When 1-octanol is completely consumed the working-state morphology of ion exchange resins changes, which influences the selectivities towards products. At this point, for microporous resins all reactions stop while with macroreticular ones DNOE decomposes and significant amounts of olefin dimers appears. The best selectivity to DNOE was found in gel-type and macroreticular resins with low crosslinking degree. Macroreticular resins with medium or high crosslinking give good results in olefin formation.

1. Introduction

Currently European oil industry is making a big effort to adapt the production facilities to maximize the gasoil production and, at the same time, improve its quality, as a consequence of the following facts: the excess gasoline-production capacity; the severe specifications ruled by the 2003/17/EC directive involving cetane number, distillation curve, viscosity, density, cold fuel properties and sulphur content; and the introduction of bio-compounds in the fuel composition ruled by 2009/28/EC and 2009/30/EC directives. An option to upgrade the quality of diesel fuel and fulfil such requirements is the reformulation of gasoil composition by adding suitable oxygenated compounds. Reformulated fuel diesels are expected to have a higher cetane number, lower density, and a lower content of aromatics, PAH (polycyclic aromatic hydrocarbons) and sulphur contents [1].

It is a well-known fact that blending linear symmetric ethers containing more than nine carbon atoms to commercial gasoil upgrades the quality of the diesel blend [2]. As shown in Table 1, thanks to their high cetane number and fluid properties, DNOE is a good candidate for enhancing blending cetane numbers resulting in a cleaner combustion of diesel fuel and, consequently, in a substantial reduction of pollutants emissions.

In addition to those properties highlighted, blends of ethers and

diesel fuels were evaluated from the perspective of fuel performance, stability and material compatibility [3,4]. Finally, it is to be noted that due to the dilution effect, the sulphur and aromatic polycyclic compounds content decreases.

The main pathway of obtaining linear ethers such as DNOE is the dehydration of the corresponding linear alcohol, 1-octanol in this case. There are several synthesis pathways for obtaining such linear alcohol. One of this is the oxo process by hydroformylation of linear olefins (1-heptene) from fluid catalytic cracking. Another way of preparing 1-octanol industrially is by ethylene oligomerization using triethylaluminum followed by oxidation of the alkylaluminum products (Alfol-process). Both petrochemical process might be an option to upgrade refinery streams [5]. Low temperature Fisher-Tropsch syncrude from gas-to-liquid facilities can be also a source of 1-octanol [6]. On the other hand, 1-octanol is a byproduct of ethanol oligomerization on hydroxyapatite [7]. If used ethanol was produced via biomass fermentation, DNOE could acquire the category of bioether and could be considered as a renewable energy source. Promising works involving 1-octanol synthesis are being developed which uses the biomass-derived platform molecule furfural and acetone [8] and microbial production of 1-octanol from glucose [9].

Intermolecular dehydration of primary alcohols to give linear ethers takes place easily in presence of acid catalysts [10]. Considering the

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Nomenclature			
S_{Bethers}	Selectivity to branched ethers (%)	T_{max}	Maximum temperature operation
S_{Dimers}	Selectivity to dimers (%)	V_{g}^{f}	Absorption of N_2 , pore volume (cm^3/g)
S_{DNOE}	Selectivity to DNOE (%)	V_{g}	ISEC pore volume (cm^3/g)
S_{Olefins}	Selectivity to olefins (%)	V_{sp}	Specific volume of the swollen polymer phase (cm^3/g)
S_{g}	ISEC surface area (m^2/g)	Y_{DNOE}	Fractional yield to DNOE (%)
S_{g}^{c}	BET surface area (m^2/g)	Acronyms	
t	Time (h)	DNOE	Di- <i>n</i> -octyl ether

advantages of using acid solid catalysts, some research work on DNOE was conducted in liquid phase over ion exchange resins catalysts without formed water removal [11–13]. Over zeolite beta, 1-octanol dehydrates selectively to octenes [14]. Zeolita Beta and Nafion-H have been also tested in liquid phase by using batch reactor equipped with a Dean & Stark device for formed water removal. On Nafion-H, 1-octanol conversion at 418–423 K was 97% and selectivity to DNOE was 100% [15]. Despite this excellent result, the industrial use of Nafion-H is economically questioned, because its price might be more than one order of magnitude respect to sulfonated resins at lab scale. Increasing interest in biomass valorization has also triggered a research for new catalytic routes to transform biomass-based derivatives in octyl-ethers to be used as transportation fuels. Thus, two catalytic routes have been recently proposed for the synthesis of bio-based long alkyl chain ethers: the telomerization of 1,3-butadiene with biomass-based glycols affords linear octyl ethers with high yields (up to 80%) using a homogeneous Pd-based catalyst; and the direct etherification with long linear alkenes with H-Beta zeolites [16].

As aforementioned [11–13], ion exchange resins could be a suitable catalyst for the synthesis of di-*n*-octyl ether. However, in the range 413–453 K it takes tens of hours to get the equilibrium conversion (higher than 96%) with selectivities to DNOE higher also than 95% for some resins. By-products found were octenes and very small amounts of branched ethers. It would be necessary a temperature rise to increase the reaction rate to an appropriate level for industrial purposes. Unfortunately, literature quoted above shows that a suitable temperature for higher linear alcohols dehydration reaction (> 423 K) to linear ethers is greater than the maximum operational temperature for standard acidic resins. Another drawback to be considered is that etherification on acidic ion exchange resins is inhibited by water, which is a reaction product from the alcohol etherification reaction and from alcohol dehydration to olefins [17].

One aim of the present work is to find the experimental conditions and the catalyst that allow to increase the ether production by dehydration of higher linear alcohols catalyzed by acidic ion exchange resins. Continuous water removal would shift equilibrium conversion to total conversion. Experimental work will be performed in a bath reactor equipped with a Dean & Stark device for water removal.

Table 1
Properties of DNOE as diesel fuel.

	Diesel fuel	DNOE
Density at 288–293 °C (kg/m^3)	850	806
Boiling point (K)	443–653	559
Viscosity (cSt)	3–4	–
Cetane number ^a (–)	48–51	119
Cloud Point ^a (K)	271–278	256
Cold Filter Plugging Point ^a (K)	269–276	258

^a Blending values.

2. Experimental section

2.1. Chemicals

1-Octanol (99.5% pure, GC), 1-(octyloxy)octane or DNOE (99% pure, GC) and 1-octene and 2-octene (> 97% pure, GC) were supplied by Across Organics, Sigma Aldrich and Fluka, respectively

2.2. Catalysts

As catalysts gel and macroreticular acidic resins will be used to check their performance in the circumstances above mentioned for 1-octanol dehydration. The tested catalysts were acidic polystyrene-divinylbenzene (PS-DVB) based resins: Amberlyst 15 (A-15), Amberlyst 16 (A-16), Amberlyst 35 (A-35), Amberlyst 36 (A-36), Amberlyst 39 (A-39), Amberlyst 46 (A-46) and Amberlyst 70 (A-70) from Rohm and Haas; Purolite CT-175, CT-224, CT-252, CT-276 from Purolite; and Dowex 50x4 (DOW50Wx4) 200–400 mesh from Aldrich. They have been chosen to cover a wide range of macroreticular and gel-type resins properties and characteristics. The resins were delivered in wet form. They were activated at 383 K, first at atmospheric pressure and then overnight under vacuum at the same temperature. Final water content after drying was less 3% w/w (Karl-Fisher titration). Commercial particles sizes were used in all the experiments.

2.3. Apparatus

The experiments were carried out in a 1 L glass batch reactor at atmospheric pressure. One of the openings was connected to a reflux consisting of a Dean & Stark burette to separate the produced water and a condenser cooled by water. Another opening was used to fit the temperature probe. The reactor was heated to boiling point of the mixture and stirred using a heat-stir supplied by Stuart (model SB162).

2.4. Analysis

Liquid samples, taken from the of reactor after finishing experiment, were analysed in a gas chromatograph (Hewlett-Packard GC 6890A) equipped with a TCD detector, that allows to measure the water content, using a 50 m × 0.2 mm × 0.5 μm methyl silicone HP 90915-001 capillary column. It was temperature programmed with 6 min initial hold at 45 °C followed by a 30 °C min⁻¹ ramp up to 180 °C and held for 5 min. Helium was used as carrier gas at a total flow rate of 30 mL min⁻¹.

2.5. Procedure and calculations

400 g of 1-octanol and 9 g of dry catalyst were charged into the reactor, stirred (700 rpm) and heated to the desired temperature. Initial time of experiment was chosen when the reacting mixture began to boil. Vapours were cooled and condensed in a Dean & Stark burette. Water, 1-octanol and olefins were collected and the organic phase (mainly 1-octanol) was returned to the reactor. The experiment finished when the separated water amount equalled that estimated by

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