



# 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).

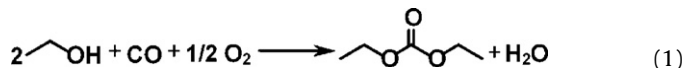
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## 1. Introduction

In order to reduce the environmental impact of diesel exhaust emissions (particulate matter, unburned hydrocarbons, CO and NO<sub>x</sub>), 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.



A drawback to use alkyl carbonates is that their decomposition generates CO<sub>2</sub> as a by-product. However, the formation of carbonates from CO<sub>2</sub> 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<sub>2</sub> 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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