



# Flow reactor synthesis of cetane-enhancing fuel additive from 1-butanol



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## ABSTRACT

The catalytic dehydration of 1-butanol on  $\gamma$ -alumina, zeolites, and Amberlyst ion-exchange resins for the production of di-*n*-butyl ether (DBE) in a fixed-bed flow reactor was studied at 130–300 °C and 1–70 bar. The activity and selectivity of the catalysts were evaluated, and the effects of operating parameters ( $T$ ,  $p$ , and  $VHSV$ ) on the kinetics of the test reaction were studied for the most active catalyst samples. Based on mass balance data, a conclusion was made that zeolites and Amberlyst ion exchangers are suitable catalysts for DBE production from 1-butanol; at a feed conversion of about 70%, selectivity for DBE was 90%. These DBE yields are reported for the first time to be obtained in a fixed-bed flow reactor.

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## 1. Introduction

The development of efficient methods for biomass conversion into fuel components and valuable chemical products is a problem of considerable current interest. The main advantages of biofuel are reduced environmental pollution and the possibility of a transition to partially carbon-neutral fuels.

Bioderived components (such as bioalcohols) are successfully used as fuel additives. The Directive 2009/28/EC sets out a common framework for the promotion of the use of energy from renewable sources in the European Union, and this is also a general trend in other countries. Bioalcohols (bioethanol and biobutanol) and fatty acid methyl esters are the main green fuel additives for gasoline and diesel fuel, respectively. A demand for high quality and ecologically clean diesel fuel is responsible for a search for compounds prepared from biomass to be used as additives in order to improve the performance characteristics of diesel fuel. Di-*n*-butyl ether (DBE) is an example of these compounds.

In contrast to other di-*n*-alkyl ethers, DBE is a bio-derived one, since it can be obtained from biobutanol, a product of the fermentation of carbohydrate-containing biomass. DBE noticeably improves the properties of diesel fuel to increase the cetane number [1] and to favorably affect antiwear properties [2], the composition of exhaust gases, and low-temperature properties [1,3]. DBE as a potential fuel additive

possesses an attractive combination of physicochemical properties: a low solidification point (−95 °C), a reasonable heat of vaporization (45 kJ/mol), and a sufficiently high net heating value (41 MJ/kg) [4]. DBE is almost immiscible with water (300 mg/L at 25 °C [4]); therefore, this additive cannot cause the settling of diesel fuel. Because of its high cetane number (100–105) [5], DBE can be used for increasing the cetane number of fuel. Harvey and Meylemans [5] reported the results of testing fuel compositions based on biobutanol (cetane number of about 25), in which DBE was a high-cetane component.

The reaction was studied on various heterogeneous catalysts, among which are aluminas [6,7], amorphous aluminosilicates [8–10], zeolites [9], sulfonic cation-exchange resins [11], aluminum phosphate [12], supported [13] and unsupported [14] heteropoly acids, and niobium silicate [15]. Some of these catalysts proved to be suitable for selective alcohol etherification, particularly sulfonated ion-exchange resins and zeolites allowing to obtain DBE with reasonable yields. Other acid catalysts (for example, niobium silicate) are better to be used for selective intramolecular dehydration of the alcohol to olefins. The main goal of the majority of these studies was to examine the mechanism of catalysis for each particular catalyst in detail. In some classic works [7–9] 1-butanol dehydration was considered to be a convenient method to test the catalytic behavior of various catalysts along with ammonia TPD and adsorbed pyridine FTIR. However, the reaction was generally performed either in GC-integrated microreactors or in stirred autoclave reactors. Of course, the experimental data obtained in these systems provide valuable information on the kinetics and mechanisms of chemical reactions; however, these data can be extended to flow systems only with considerable limitations. At the same time, fixed-bed flow

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reactor is known to be a simple and robust system for industrial-scale process realization. Etherification in flow systems was previously reported several times. Nel and De Klerk [16] studied C<sub>5</sub>–C<sub>12</sub> alcohol dehydration over  $\eta$ -Al<sub>2</sub>O<sub>3</sub> (flow reactor, 10 g of catalyst load) and achieved 54% of linear ether yield; maximum ether selectivity did not exceed 75%. Brandao et al. [15] carried out dehydration of ethanol, 1-propanol and 1-butanol over microporous niobium silicate (flow microreactor, 0.05 g of catalyst load), which proved to be an excellent catalyst for intramolecular dehydration of 1-butanol whereas selectivity for DBE was low. Finally, Cunill et al. [17] performed 1-pentanol dehydration in a continuous autoclave reactor (internal volume 100 cm<sup>3</sup>) over CT-224 ion-exchange resin. Alcohol conversion kinetics was discussed in detail, but maximal yield of the linear ether did not exceed 25%.

Previously reported results on DBE heterogeneously-catalyzed synthesis are summarized in Table 1. As it can be seen, maximal yield of DBE was reported to be about 33 mol% [18]. The experiment was carried out in the flow of supercritical carbon dioxide. Also, there are data which show that DBE yield reach 72% when catalyzed by H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> heteropolyacid [14]. These impressive results were not taken into account here since they correspond to a homogeneously-catalyzed reaction. Note that not one of the authors listed in Table 1 used a flow reactor with a volume higher than 10 cm<sup>3</sup>.

1-Butanol conversion is highly dependent on the phase composition of the reaction mixture having crucial influence on the reaction selectivity. The reaction is reported to be previously realized in both gaseous and liquid phases. Pressurizing the reaction mixture yields higher ether selectivity (the direct consequence of Le Chatelier's principle). The previous works could be divided into two groups: 1) gaseous phase conversion of 1-butanol vapor diluted by helium in a GC-integrated flow microreactor [6–9,19], 2) liquid-phase conversion of 1-butanol in liquid phase pressurized with nitrogen [11], under autogenerated pressure [20] or as a solution in supercritical carbon dioxide [18]. Solventless conversion of alcohols was reported by Ballantine [20] for 1-butanol (batch reactor) and by Nel and De Klerk [16] for C<sub>5</sub>–C<sub>12</sub> alcohols (flow reactor). To the best of our knowledge the latter study is the only one containing the investigation on the pressure effect. Moreover, we did not find any information about heterogeneous conversion of neat 1-butanol in a continuous reactor.

Regarding the aforesaid, today we do not have any reliable information about conversion of butanol-1 into DBE in a flow reactor with high yields.

Because we believe that DBE is a promising renewable component of diesel fuel, we studied in detail the production of this fuel additive under nearly industrial conditions and performed its synthesis in a fixed-bed flow reactor. Since the main goal of this study was to find a combination of maximum DBE yield and selectivity, the results obtained may be useful for further process scaling. Ultimately the development and industrial realization of DBE synthesis process might be a step on the road to cleaner motor fuels production and to wider involving of biomass into fuel production.

## 2. Experimental

### 2.1. Materials

1-Butanol (99% purity, Aldrich) was used without further purification. Commercial thermally stable macroporous styrene-divinylbenzene ion-

exchange resins Amberlyst 36 DRY and Amberlyst 70 (Rohm & Haas, France),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Ryazan Catalyst Factory, Russia), and Tseokar-600 (Salavat Catalyst Factory, Bashkortostan, Russia) were used as catalysts. Zeolites BEA (CP814E) and USY (CBV 760) from Zeolyst International (Kansas City, Kansas, USA) were used after calcination at 550 °C for 10 h. Sulfonic exchange resins were used after drying under vacuum (20 mmHg) at 90 °C during 6 h. Table 2 summarizes the properties of the test catalysts (data for the Amberlyst catalysts refer to an unswollen state).

The amount of acid sites of catalysts was determined by acid–base titration. A weighed sample was vigorously stirred in a 10% NaCl aqueous solution over 4 h, then the solid phase was filtered off and the solution was titrated with 0.01 mol/L NaOH (with phenolphthalein as the indicator). Data on the total acidity of zeolites and ion-exchangers were provided by suppliers and further confirmed by means of this method.

Other physical properties were obtained from the producers.

### 2.2. Apparatus

The catalytic experiments on butanol conversion were performed with the use of a laboratory flow system (Fig. 1). This flow system consisted of (1) a feed flask, (2) a Gilson 305 HPLC pump, (3) an electrically heated catalytic fixed-bed reactor (120\*20 mm), (4) a condenser, and (5) a separator.

The temperature conditions were controlled with two thermocouples (at the center of the catalyst bed and at the reactor wall) and a thermoregulator. The reactor pressure was tuned by a Swagelok backpressure regulator and controlled by two manometers at the reactor inlet and at the reactor outlet. The gaseous reaction products from the separator were vented to a flare through a bubble gage.

### 2.3. Analysis

The composition of the products of catalysis obtained after a 4-h operation of the flow system was determined by gas–liquid chromatography (GLC) on a Kristalyuks-4000 M chromatograph with a flame-ionization detector using a Supelco SPB-1000 (30 m × 0.25 mm) column. The analysis was performed under temperature programming conditions including an isothermal exposure at 60 °C (5 min), a temperature rise from 60 to 160 °C at a heating rate of 30 K/min, and a 10-min exposure at 160 °C.

Since FID detectors are unable to detect water concentration, it was calculated from the material balances starting from the statement that each molecule of water is formed per one molecule of dehydration product (e.g., ether, olefin or oligomer).

The structure of the reaction products was determined by gas chromatography–mass spectrometry (GC–MS) analysis on a Finnigan MAT 95 XL instrument (Varian VF-5 ms capillary column, 30 m × 0.25 mm). Helium was used as a carrier gas. The injector temperature was 270 °C, and the initial column temperature was 30 °C; after an isothermal exposure for 5 min at this temperature, the column oven temperature was increased to 300 °C at a rate of 10 K/min. The ionization energy was 70 eV, and the source temperature was 230 °C. Scanning over a range of 20–800 Da was performed at a scan rate of 1 s per decade at 1000 resolution. The components were identified

**Table 1**  
Previously reported DBE heterogeneous conversion results.

Catalyst	T, °C	p, bar	X <sub>BuOH</sub>	S <sub>DBE</sub>	Y <sub>DBE</sub>	Reactor type	Reference
S/ZrO <sub>2</sub>	180	1	38	10	4	Flow microreactor	[19]
A-36	150	40	23	96	20	Batch stirred	[11]
Al <sup>3+</sup> -exchanged montmorillonite	200	Autogen	56	45	25	Batch stirred	[20]
Deloxan ASP	200	200	–	–	33	Supercritical flow reactor	[18]

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