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Continuous catalytic coupling of raw bioethanol into butanol and higher homologues

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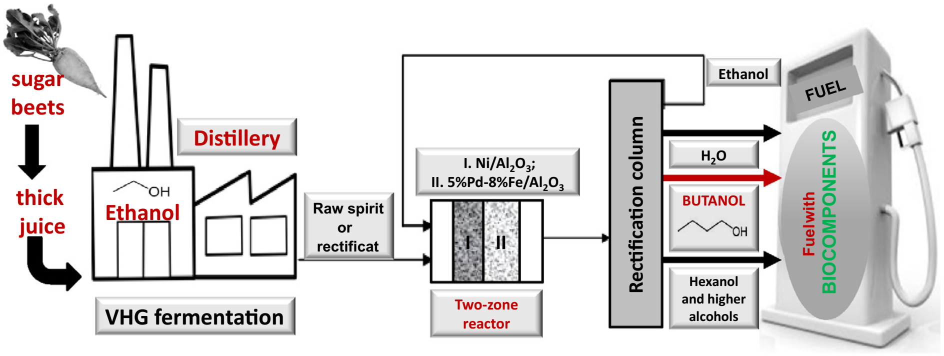
HIGHLIGHTS

- Condensation bioethanol was successfully performed over 8–20%Ni/Al_2O_3 catalysts.
- 20%Ni/Al_2O_3 yielded almost 13% butanol after a single passage of bioethanol at 330 °C, 120 atm.
- The use of a two-zone reactor allowed the system to operate under milder pressure (80 atm) and temperature (290 °C) condition.
- The results of the studies suggest the possibility of using continuous-flow technologies for the industrial-scale.

GRAPHICAL ABSTRACT



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ABSTRACT

Continuous catalytic condensation of crude distillates or rectified bioethanol into butanol and other fuel bicomponents was performed over 8–20%Ni/Al_2O_3 catalysts. Experiments were conducted using solid catalysts in a flow reactor under supercritical conditions. The most promising nickel catalyst yielded almost 13% butanol after a single passage of the raw spirit or rectified ethanol at 330 °C, 120 atm. The butanol content in the liquid products was further increased to 31.4% (v/v) by the additional step of rectification and recycling of the low-boiling fraction through a catalytic reactor. The use of a two-zone reactor filled with different catalytic systems (I. 8%Ni/Al_2O_3; II. 5%Pd-8%Fe/Al_2O_3) allowed the system to operate under milder pressure (80 atm) and temperature (290 °C) conditions, while maintaining approximately 13% (v/v) of the butanol content in the reaction mixture. The results of the studies suggest the possibility of using continuous-flow technologies for the industrial-scale catalytic condensation of bioethanol into butanol and higher homologues, which are valuable fuel biocomponents.

1. Introduction

The first and to date most successful approach to biofuel fabrication is based on ethanol, which can be produced highly efficiently using the classic fermentation process. This method is already used on a large scale in Brazil, where bioethanol supplies 40% of the fuel used by cars and buses. Additional benefits are the low cost solar energy harvesting and sequestering and recycling of atmospheric carbon dioxide that occur as part of the photosynthetic bioprocess.

Unfortunately, ethanol has several disadvantages, which severely limit its application as an alternative fuel for cars, or even as a fuel additive. Ethanol (E100) consumption in engines is

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approximately 51% higher than with gasoline, since the energy per unit volume of ethanol (energy content for ethanol –19.6 MJ/L) is 38.75% lower than that of gasoline (32 MJ/L) [1]. This may be partially compensated for by the higher compression ratio in ethanol-only engines, which increases power output and improves fuel economy compared with standard lower compression engines. Nonetheless, current high compression engines are still approximately 20–30% less fuel efficient than their gasoline-only equivalents. Moreover, as a fuel additive ethanol can be used only in relatively low concentrations, if the standard parameters of the fuel are to be approximately maintained, and the need to modify the car's engine avoided.

Given the shortcomings of ethanol as a universal fuel, or even as a component in fuel blends, biobutanol and higher alcohols are seen by some as promising alternatives [2]. First of all, the calorific value of butanol is higher than that of ethanol (the energy content for butanol is 29.2 MJ/L). It is also fully miscible with gasoline and diesel, has lower miscibility with water, a higher octane number (96 RON) and lower volatility. Because of its higher hydrophobicity, it can be preserved under humid conditions, and its noncorrosive properties enable mixtures with gasoline of up to 30% (v/v) to be used in existing combustion engines without requiring modifications [3].

What is more, butanol may be obtained by fermentative method with the using of Clostridia strains from various bioresources [4,5]. As a result of this biological route the mixture acetone–butanol–ethanol (ABE) is produced. However, ABE fermentation has some problems such as high cost of fermentation substrate, serious inhibition by butanol and low butanol concentration in the product [6]. All these limitations result in low butanol productivity, co-fabrication of additional by-products, high downstream processing cost for butanol recovery, the formation of mixed solvents and relatively low butanol content in the crude product. To develop economical and sustainable processes for bio-based butanol production, attempts were made to modify the metabolic pathways of native Clostridia microorganisms [7–9]. Limited attention has been paid to the distillation process in the production of acetone/biobutanol by ABE method and its optymalization [10]. The results obtained by Sanchez–Ramirez et al. [11] indicated that the process consisted of a liquid–liquid equilibrium (LLE) column followed by stream stripping distillation may be a profitable in current economic conditions. Another way to the obtained a biobutanol from biomass by ABE method is the use of alternative product recovery techniques, eg adsorption, gas stripping, ionic liquids and others [12]. For example, Kubiczek and Kamiński [13] stated that ionic liquids like 1-hexyl-3-methylimidazolium hexafluorophosphate and 1-hexyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide efficient recovery of n-butanol from aqueous solutions when volume of both liquids are approximately equal. These alternative processes can be employed in future on an industrial scale to improve the process economics of biobutanol production.

However currently, most butanol is fabricated via chemical pathways based on oxo synthesis, Reppe synthesis or crotonaldehyde synthesis followed by hydrogenation. However, none of these methods is cost-effective for the industrial-scale manufacture of butanol as a fuel component. A more promising approach involves the transformation of easily accessible bioethanol into butanol. However, in the classic chemical multistep procedure, proceeding from acetaldehyde condensation into crotonaldehyde followed by hydrogenation, as well as in one-step catalytic transformation, the crude fermentation product must first be dehydrated until it reaches the 100% anhydrous state before it can be used as a substrate [14].

The aim of the studies presented here was to develop a continuous process of bioethanol condensation using rectified spirit (96% ethanol) and crude distillates (not purified from other fermentation products). These distillates were produced by fermentation of high gravity thick sugar beet juice worts, which was described in our previous report published in Biotechnology for Biofuels [15]. Under the favorable conditions determined in those work, 38.9 ± 1.2 L of 100% (v/v) ethyl alcohol can be produced from 100 kg of thick juice. What is more, these distillates are produced in commercial distilleries and could be used directly in on-line continuous processes for the industrial-scale production of butanol.

2. Methods

2.1. Catalytic studies of nickel supported catalysts

2.1.1. Catalyst preparation

Catalysts containing 8–20 wt.% nickel were prepared by impregnating Al_2O_3 (Fluka, 143 m^2/g) with an aqueous solution of $Ni(NO_3)_2 6H_2O$ (POCH, pure p.a.). The water was evaporated at an elevated temperature ($T = 60$ °C) under a vacuum. Monometallic 8–20%Ni/Al_2O_3 catalysts were dried in air at 110 °C for 6 h, calcined at 500 °C for 4 h in an oxygen atmosphere (O_2, Air Products, 99.5%, at a rate of 20 mL min^{-1}), cooled in argon to room temperature (Ar, Linde 5.0, at a rate of 20 mL min^{-1}), then reduced in a hydrogen atmosphere (H_2, Air Products, Premium Plus, 99.999%, at a rate of 20 mL min^{-1}) for 2 h at 500 °C before catalytic measurements were taken. The linear temperature increase rate was 20 °C min^{-1} between each thermal processing step.

A bimetallic 5%Pd–8%Fe/Al_2O_3 catalyst was prepared by co-impregnation of Al_2O_3 with a water solution of $Fe(NO_3)_3{\cdot}9H_2O$ (POCH, pure p.a.) and $PdCl_2$ (POCH, anhydrous, pure p.a.) acidified to around pH 5 using $HCl_{(aq)}$ (CHEMPUR, 35–38%, pure p.a.), according to the procedure described above.

2.1.2. Catalytic measurements

Experiments were carried out in a continuous fixed-bed tubular reactor (10 mm id, 240 mm length) mounted horizontally in our own design of electric furnace, as presented in Fig. 1. 20.3 g of 8%Ni/Al_2O_3 or 23.3 g of 20%Ni/Al_2O_3 of pre-reduced (300 °C, 2 h, H_2 99.999%) home-made catalyst was loaded into a high-pressure flow reactor heated to a temperature of between 200 and 400 °C. Directly into the catalyst bed, three Type K (chromel–alumel) thermocouples were installed at the beginning, in the middle and at the end of the reaction chamber, which allowed for precise control of the temperature in the ethanol coupling process. During the experiments we did not notice the local overheating effects in the catalyst bed. Raw spirit (83% ethanol) obtained from the fermentation of thick sugar beet juices containing ethanol (among other post-fermentation components), rectified spirit (96% ethanol) obtained from the raw spirit and commercial absolute alcohol (>99% ethanol) were pumped at a volumetric flow rate of 2.4 mL min^{-1} under a pressure of 20–120 atm. The reaction mixture was discharged from the reactor into the high pressure cooler, where it expanded and before being placed in the low-pressure condenser. The liquid reaction products of ethanol coupling were screened for using GC–FID analysis (Perkin Elmer Clarus 580; column ZERBON ZB-5MS (30 m, 0.25 mm i.d., 0.5 μm); injection port temperature: 150 °C, injection volume: 5 μl; split 1:200, FID detector temperature: 280 °C; He (Linde, 99.999%): 30 cm s^{-1}).

Analysis of the reaction mixture components was performed according to the temperature program: 35 °C (5 min) to 155 °C (1 min) with a temperature increase of 10 °C min^{-1}. The products were in additionally analyzed using a Perkin Elmer Clarus 580 GC-MS system (MS Clarus SQ 8 S) equipped with an Elite-5MS capillary column (30 m, 0.25 mm i.d., 0.5 μm). The operating