

CATALYTIC CONVERSION OF BIO-ETHANOL INTO BUTANOL

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Abstract

In this paper the catalytic conversion of ethanol produced by ABE fermentation of Agrofood waste (AFW) into a more valuable bio-fuel, as butanol, is reported. The process involves the dimerization of ethanol to butanol, generally known as Guerbet reaction. A lab-scale rig has been developed for the screening of heterogeneous catalysts suitably synthesized for the conversion of ethanol into butanol. Catalysts with different surface properties have been prepared in order to investigate the effect of the presence of acid and basic surface sites coupled with the addition of small amounts of an active metal (Ru, Ni) providing hydrogenation - dehydrogenation properties

Introduction

In the next decades one of the most challenging problems Europe will address is the production of energy through low-carbon technologies. The production of sustainable biofuels is related to the low-cost, large availability and supply, reasonable transportation and upstream processing costs of raw materials. Agrofood waste (AFW) represents one of the main sources since each year in the European Union (EU) 89 million tonnes of food waste are produced.

As a consequence, the development of novel technologies or the improvement of the existing ones to convert AFW into high quality biofuel, in particular bio-butanol, for use as a direct substitute for fossil fuels is strongly required. Actually, bio-butanol is one of the most promising alternatives for fuel markets having some advantages compared to ethanol that, on the other hand, is water soluble and corrosive for internal combustion engines. Butanol can be burned in the existing gasoline engines without practically any engine or car modifications, it has higher energy content and air-to-fuel ratio and can be distributed via the existing pipelines for gasoline. It can be obtained through ABE fermentation but with low yields. Consequently, processes of valorization of ethanol produced by fermentation into butanol should be developed.

Synthesis of higher alcohol from lower alcohol is generally known as the Guerbet reaction occurring through an indirect process in which ethanol is converted to *n*-butanol via acetaldehyde [1, 2]. The process must be catalyzed in order to drive the reaction path towards the production of butanol instead of other by-products. A suitable combination of both acid and basic sites is considered a key-feature for an

effective catalyst. Furthermore, addition of an active metal capable to provide hydrogenation/dehydrogenation properties might promote the initial dehydrogenation of the alcohol to form the carbonyl intermediate of the Guerbet coupling [1, 2, 4, 5].

In this work, a lab-scale rig has been developed for the screening of heterogeneous catalysts suitably synthesized for the conversion of ethanol into butanol. Catalysts with different surface properties have been prepared in order to investigate the effect of the presence of acid and basic surface sites coupled with the addition of small amounts of an active metal (Ru, Ni) providing hydrogenation - dehydrogenation properties. This work has been done in the framework of the research project Waste2Fuels 'Sustainable production of next generation biofuels from waste streams' (N. 654623) funded under the European Union's research and innovation program Horizon 2020.

Development of the lab-scale rig.

Catalytic tests have been carried out in a lab-scale rig in order to select the most performing catalyst and to determine the more suitable operating conditions. Catalytic test were carried out in the temperature range 200-500°C by feeding an (2.5-3% vol.) ethanol/N₂ mixture to a fixed bed reactor of powdered catalyst (300-400 μm). Reactants and products can be analysed by an online GC equipped with FI detector.

A sketch of the test rig is presented in Figure 1. The reactor is operated at nearly atmospheric pressure, under pseudo-isothermal conditions. An ethanol/N₂ mixture is prepared by mixing two N₂ streams, independently regulated by mass flow controllers, one of which passes through an ethanol saturator hold at room temperature. Gas lines connecting reactor with GC are heated in order to avoid products condensation before analysis.

Performance of catalysts with different acid/base and redox properties have been tested in order to select the best materials to be reproduced in form of pellets or spheres for a pre-pilot scale rig developed by HELBIO which is another partner of Waste2Fuels project.

The catalytic systems to investigate are based on hydroxyapatite (HAP), MgO or γ -Al₂O₃ as supports. Moreover, the effect of the dispersion of small amounts ($\leq 1\%$) of active metal such as ruthenium or nickel has been studied.

Both supports and Ru and Ni-based catalysts have been characterized by XRD, N₂ physisorption, TGA, CO₂ and NH₃ TPD, H₂ TPR in order to associate the best performance to specific physico-chemical properties.

Preliminary catalytic tests have been performed on bare supports. The main products detected are, in addition to butanol, acetaldehyde, crotonaldehyde, diethylether and ethylene.

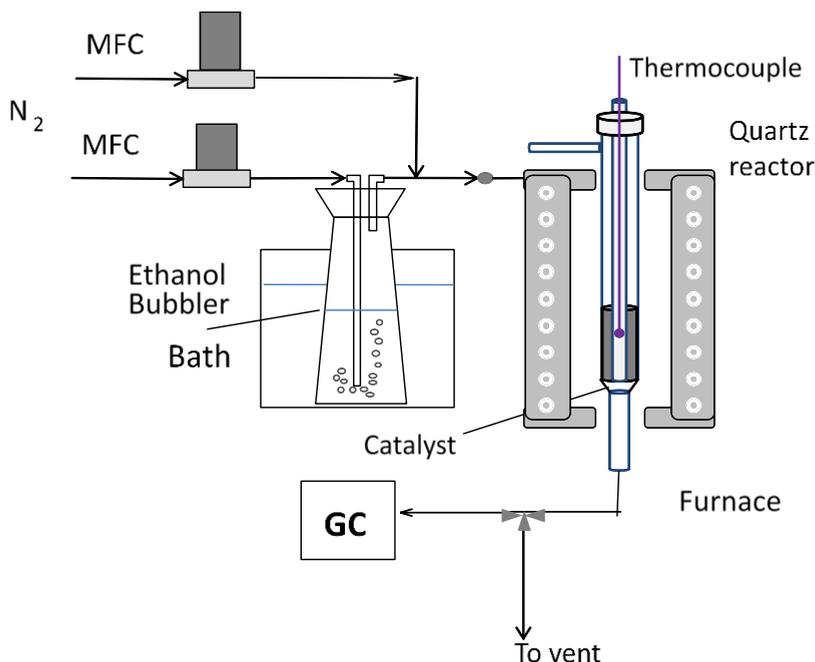


Figure 1. Sketch of the experimental rig for catalysts screening.

HAP shows a negligible activity up to 300°C whereas between 300 and 400°C an almost complete ethanol conversion has been observed that, however, is mainly involved in cracking reactions and does not produce butanol. γ -Al₂O₃, although providing a high ethanol conversion already at 300°C, also shows a cracking activity due to the large amount of surface acid sites.

On the contrary, MgO shows an intrinsic activity towards butanol production showing a maximum with temperature at about 450°C despite of the quite low surface area. The addition of a ruthenium does not improve performance of HAP, whereas it results in the appearance of butanol for γ -Al₂O₃ that although low, suggests a key-role of the metal. Dispersion of a small fraction of Ru or Ni increases ethanol conversion and butanol selectivity.

Long run tests at the temperature of maximum ethanol yield have been carried out in order to verify the stability of the materials.

The activity is currently devoted to dispersion of the most performing materials (Ru or Ni-promoted MgO) on alumina pellets. Several cycles of impregnation have been performed in order to obtain a complete coverage of the alumina pellets thus exposing totally MgO surface.

References

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