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Butanol production in a sugarcane biorefinery using ethanol as feedstock. Part I: Integration to a first generation sugarcane distillery

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ABSTRACT

Butanol production from renewable resources has been increasingly investigated over the past decade, mostly for its use as a liquid biofuel for road transportation, since its energy density is higher than that of ethanol and it may be used in gasoline driven engines with practically no changes, but also for use as a feedstock in the chemical industry. Most of the research concerning butanol production focuses on the ABE process (fermentation of sugars into a mixture of acetone, butanol and ethanol), which has several drawbacks regarding microorganism performance and product inhibition. An alternative to ABE fermentation, ethanol catalytic conversion to butanol can produce a higher quality product with less retrofitting than ABE in existing ethanol producing facilities. There are different types of catalysts for the chemical conversion of ethanol to butanol being developed in laboratory scale, but their actual use in a sugarcane processing plant has never before been assessed. Butanol production from ethanol in a sugarcane biorefinery, using data from the literature, was assessed in this study; different technological alternatives (catalytic routes) were evaluated through computer simulation in Aspen Plus (including production of electricity, sugar, ethanol and other products) and economic and environmental impacts were assessed. Results indicate that vapor-phase catalysis presents higher potential for industrial implementation, and commercialization of butanol for use as a chemical feedstock has an economic performance similar to that of current, optimized first generation sugarcane distilleries, but can potentially contribute to cost reduction that will allow commercialization of butanol as a fuel in the future.

Keywords: Butanol; Ethanol; Alcoholchemistry; Simulation; Economic analysis; Life cycle assessment

1. Introduction

Different biorefinery routes for production of biofuels and chemicals can be envisioned today. Among liquid biofuels for transportation, ethanol has been extensively studied, and it is used in large scale in countries like Brazil and United States. Other products may be used as fuels as well; n-butanol has received a lot of attention, since it has higher energy content than ethanol and may be used in current gasoline driven engines with practically no changes in engines and cars

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(Riittonen et al., 2012). In addition, n-butanol is an important feedstock for the chemical industry, being used in paint, solvents and plasticizers production (Carvalho et al., 2012). Most of the n-butanol produced in the world is derived from oil; development of renewable chemicals to replace fossil-derived feedstock in the chemical industry is essential, considering the depletion of fossil resources, global warming as well as other environmental impacts related to the use of fossil fuels (Brehmer et al., 2009; Mariano et al., 2013).

Butanol production from renewable resources usually considers the ABE (acetone–butanol–ethanol) fermentation of sugars, such as sucrose derived from sugarcane. This process has been extensively studied but faces some technological challenges: low productivity and low n-butanol concentration in the reactor due to product inhibition, among the most important. To overcome these obstacles, mutant strains able to tolerate higher n-butanol concentrations have been developed (Mariano and Maciel Filho, 2012). The use of these mutant strains in the Brazilian sugarcane industry, however, is viewed with caution, since aseptic conditions and total confined environment must be created and maintained during the entire fermentation process. In addition, converting ethanol fermentation plants to n-butanol (ABE) fermentation would require costly modifications (ACS, 2013).

Another route that may be potentially viable to produce n-butanol from sugarcane is the alcoholchemistry (or ethanolchemistry) route, in which ethanol is used as feedstock in catalyzed chemical reactions. The ethanolchemistry industry played a significant role in Brazil during the oil crisis in the 1970s, up until the late 1980s, when oil prices went back down. The most important products derived from ethanol at that period were dichloroethane, polyethylene and acetaldehyde (Rosillo-Calle, 1986). In the past few years, uncertainties regarding oil prices and the search for increased sustainability of the chemical industry have motivated the renaissance of the ethanolchemistry industry in Brazil: Braskem is now the world's largest producer of green polyethylene, made from sugarcane derived ethanol, having a commercial scale plant in operation since 2010 (Braskem, 2013).

Using ethanol as feedstock for n-butanol production would require less retrofitting than replacing ethanol by n-butanol fermentation (ACS, 2013); thus, existing ethanol facilities could produce n-butanol by using catalysts to convert ethanol. Several studies in the literature detail the development of catalysts for this conversion (Carvalho et al., 2012; Marcu et al., 2009; Ndou et al., 2003; Riittonen et al., 2012; Tsuchida et al., 2006, 2008a; Yang et al., 2004). These studies, however, are generally limited to the evaluation of catalyst performance, providing little information on their use at commercial scale. Therefore, it is unknown whether the use of such catalysts in ethanol conversion processes provides advantages, especially in the Brazilian context, where ethanol is already largely used as a fuel and has a consolidated market and distribution network (Kostin et al., 2012). However, production of n-butanol in the sugarcane biorefinery might increase its profitability, producing a biofuel more suitable for external markets or a renewable feedstock for use in the chemical industry.

Process simulation can be used to evaluate new biorefinery configurations in a relatively fast manner, taking into consideration the complexity of the process regarding technological routes, product portfolio and biomass source, among others. It also allows the comparison of different process configurations and their impacts on the entire production process, which would be much harder to achieve in an experimental scale. In addition, process simulation can provide data required for estimation of economic (Dias et al., 2013; Franceschin et al., 2011; Macrelli et al., 2012; Mariano et al., 2013; Misailidis et al., 2009; Quintero and Cardona, 2011; Tao et al., 2011; Trippe et al., 2011; Van der Merwe et al., 2013) and environmental impacts (Cavalett et al., 2012; Ojeda et al., 2011; Seabra and Macedo, 2011; Sánchez and Cardona, 2012; Spatari et al., 2010; Walter and Ensinas, 2010). Integrating all these features, the Virtual Sugarcane Biorefinery (VSB) is an assessment tool under development at the Brazilian Bioethanol Science and Technology Laboratory (CTBE/CNPEM), through which the viability of various biorefineries configurations are evaluated according to their technical, economic and environmental impacts, coupling process simulation with economic and environmental analyses.

In this study, the production of n-butanol in a sugarcane biorefinery using first generation ethanol as feedstock within the Virtual Sugarcane Biorefinery framework was evaluated (Cavalett et al., 2012). Different technological routes (liquid and vapor phase heterogeneous catalysis) and reactor arrangements were compared.

2. Process description

An optimized first generation annexed distillery, with 50% of the sugarcane juice diverted for sugar production and the remaining 50% (plus molasses, the sugar residual solution obtained after sugar crystallization) for ethanol production, was considered for the integration of the n-butanol production process. This distillery is optimized for maximum electricity generation, using all sugarcane bagasse and 50% of the straw (sugarcane tops and leaves) as fuel in 90-bar boilers. Surplus electricity is sold to the grid. Further details about the annexed sugarcane distillery are provided in a previous work (Cavalett et al., 2012). Anhydrous ethanol (99.6 wt%) produced in the dehydration section is used as feedstock in the n-butanol plant. A simplified scheme of the biorefinery producing n-butanol from ethanol is shown in Fig. 1.

Two configurations of the catalytic process for butanol production were assessed. A brief description of the processes is provided below.

2.1. *Liquid-phase catalysis*

Riittonen et al. (2012) describe the use of liquid-phase catalysis for conversion of ethanol into n-butanol, a configuration reported for the first time in the literature. Several alumina-supported catalysts were evaluated, and the best results (25% ethanol conversion and 80% n-butanol selectivity) were obtained for commercial Ni/Al_2O_3 after 72 h of reaction at 250 °C and 70 bar. Acetaldehyde, ethyl acetate, 1-hexanol, diethyl ether, butyraldehyde and 1,1-diethoxy ethane were the detected co-products. The authors provided information on the reaction kinetics, and product concentrations were used to estimate the conversion in the reactor.

2.2. *Vapor-phase catalysis*

Among the catalysts reported in recent literature for ethanol conversion, non-stoichiometric hydroxyapatite has provided interesting results, concerning high n-butanol selectivity. Tsuchida et al. (2006) developed the highly active calcium phosphate compound for use as a catalyst in ethanol conversion with selectivity toward n-butanol as high as 76% (300 °C,