Applied Energy 160 (2015) 120–131

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Economic and environmental assessment of n-butanol production in an integrated first and second generation sugarcane biorefinery: Fermentative versus catalytic routes

L.G. Pereira [a,*], M.O.S. Dias [b], A.P. Mariano [c], R. Maciel Filho [a,c], A. Bonomi [a,c]

[a] Brazilian Bioethanol Science and Technology Laboratory (CTBE), Brazilian Center of Research in Energy and Materials (CNPEM), Caixa Postal 6192, CEP 13083-970, Campinas, São Paulo, Brazil
[b] Institute of Science and Technology, Federal University of São Paulo (ICT/UNIFESP), São José dos Campos, São Paulo, Brazil
[c] School of Chemical Engineering, University of Campinas (UNICAMP), Campinas, São Paulo, Brazil

HIGHLIGHTS

- Financial and environmental impacts of n-butanol production were investigated.
- Analysis showed promising economic results for ABE fermentation scenarios.
- Ethanol catalysis to butanol presented discouraging figures.
- n-Butanol use as fuel demonstrated favorable GHG emissions results.

ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 26 August 2015
Accepted 12 September 2015

Keywords:
n-Butanol
ABE fermentation
Ethanol catalysis
Life cycle assessment
Risk analysis

ABSTRACT

n-Butanol produced from renewable resources has attracted increasing interest, mostly for its potential use as liquid biofuel for transportation. Process currently used in the industry (Acetone–Butanol–Ethanol fermentation – ABE) faces major technical challenges, which could be overcome by an alternative production through ethanol catalysis. In this study, both routes are evaluated by means of their financial viabilities and environmental performance assessed through the Virtual Sugarcane Biorefinery methodological framework. Comparative financial analysis of the routes integrated to a first and second generation sugarcane biorefinery shows that, despite the drawbacks, ABE process for fermentation of the pentoses liquor is more attractive than the catalysis of ethanol to n-butanol and co-products. n-Butanol use as fuel demonstrated favorable environmental results for climate change as figures showed over 50% reduction in greenhouse gas emission compared with gasoline.

1. Introduction

Different biorefinery routes for the production of biofuels and chemicals are envisioned today. Among biofuels, ethanol has been extensively studied and used in large scale in countries such as Brazil and the US. Other compounds may be used as fuels as well; n-butanol has received a lot of attention and seems to be preferred over other alcohols, because of its superior fuel properties in comparison to ethanol [1] and due to its characteristics it is considered as a drop-in biofuel for Carnot cycle engines. Additionally, n-butanol is an important feedstock for the chemical industry, being used in the production of paint, solvents and plasticizers [2] with a projected global market of 5 million tonnes in 2018 [3]. China is the major consumer with 34% of the world demand, followed by Europe and North America with 25% and 24%, respectively [4].

Studies have pointed out the advantages of n-butanol as fuel in comparison with ethanol: n-butanol contains a longer hydrocarbon chain being more similar to gasoline (both are hydrophobic); may be mixed with gasoline and diesel at higher proportions [5,6]; Mendez et al. [7] concluded that blends of butanol with jet fuel present promising performance; according to Tao et al. [8], butanol fuel efficiency may equal that of gasoline; it may be used as oxygenate to allow more complete combustion, reducing carbon monoxide emissions [9]; it is capable of performing better for an

* Corresponding author. Tel.: +55 19 3518 3197; fax: +55 19 3518 3104.
E-mail addresses: lucas.pereira@bioetanol.org.br, lucgpereira@gmail.com (L.G. Pereira).

http://dx.doi.org/10.1016/j.apenergy.2015.09.063
0306-2619/

engine's cold start and may also be used as an additive to ethanol for that function [10].

Most of the n-butanol currently produced in the world is derived from oil. The development of renewable chemicals to replace fossil-derived feedstock in the chemical industry is essential, considering the forecasted depletion of fossil resources and greenhouse gas emission target [11]. Production from renewable resources usually considers the ABE (acetone–butanol–ethanol) fermentation of sugars, such as sucrose extracted from sugarcane. Recent studies have evaluated the ABE process feasibility for other feedstocks such as eucalyptus hydrolysate [12], wastewater microalgae [13] and starchy food wastes [14]. The interest renewable butanol has attracted from the chemical industry is confirmed by the construction of pilot plants and the planning of industrial scale units for production of butanol from fermentation of sugars around the world [15]. Although this process has been extensively studied, it faces major technical challenges: low butanol titers derived from microorganism inhibition towards the product leading to high recovery costs and extremely high water usage, with consequent large stillage production, and low solvent productivity [16–18]. Mutant strains able to tolerate higher butanol concentrations have been developed, but their use in the Brazilian sugarcane industry is viewed with caution, since aseptic conditions must be created, which will certainly increase investment and operational costs [19].

An alternative process that could overcome some of these drawbacks for the production of n-butanol from sugarcane is the alcoholchemical route, in which ethanol is used as feedstock in catalyzed reactions. Several studies detail the development of catalysts for ethanol conversion into butanol at laboratory scale [1,2,20–25]. These studies, however, are often limited to the evaluation of the catalyst performance, focused on improving butanol selectivity, since catalytic reactions lead to simultaneous production of various chemicals besides n-butanol. Results available in the literature provide little information on the use of catalysts at industrial scale. Therefore, it is unknown whether their use in ethanol conversion processes provides advantages, especially in the Brazilian context, where ethanol is largely used as a fuel and has a consolidated market [26].

Second generation ethanol production can significantly increase ethanol production and has been studied over the past decades, but remains facing technical and economic challenges [27]; Macrelli et al. [28]. The concept of a biorefinery, which consists of maximized biomass conversion efficiency into various products (fuels, chemicals, materials, and energy) to improve its competitiveness against fossil-derived products [29], should be applied to sugarcane processing into second generation ethanol as well. Inclusion of butanol and chemicals production in first and second generation biorefineries can add flexibility to their product portfolio and possibly increase their revenues [30].

Process simulation can be used to evaluate biorefinery configurations 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 evaluate using only experimental data. Additionally, simulation can provide data required for estimation of economic [8,17,19,31,28,32–37] and environmental performance [33,38–43]. Previous recent studies from the authors of this paper have evaluated technical aspects and economics of n-butanol production from sugarcane sugars [17,32] and ethanol catalysis [19,30,44], as well as the environmental performance of the ABE process in a sugarcane biorefinery [42].

In this study two competing technological routes for the production of n-butanol (fermentative and catalytic route) were assessed as facilities added to a sugarcane biorefinery with integrated production of first and second generation ethanol. Economic feasibility and environmental performance were determined with the aid of the Virtual Sugarcane Biorefinery tool. Uncertainties assigned to technical parameters of both technological routes as well as to the selling prices of n-butanol and co-products generated enabled the analysis of the economic risk. Life cycle assessment applied under two different approaches (economic and energy allocation) allowed the comparison of the environmental impacts of the production routes investigated as well the GHG emissions reduction associated with bio-based butanol use in the automotive fuel market context.

2. Methods

2.1. Virtual sugarcane biorefinery

Developed by the Division of Integrated Evaluation of Biorefineries of the Brazilian Bioethanol Science and Technology Laboratory (CTBE) from the Brazilian Center for Research on Energy and Materials (CNPEM), the Virtual Sugarcane Biorefinery (VSB) is a comprehensive tool able to evaluate, from a sustainability standpoint, different biorefinery configurations [45,46]. The methodological framework integrates simulation platforms and assessment methods with the objective of identifying and evaluating technical parameters and sustainability impacts (economic, social and environmental) related to the introduction of new technologies (cellulosic ethanol and green chemistry products) in current Brazilian sugarcane biorefineries.

The construction of this tool is directly focused on key scientific and technological aspects of future biorefineries, requiring the elaboration of mathematical models to be introduced in the simulation platforms. The term virtual refers to the fact that it can predict/calculate parameters of various biorefinery alternatives/routes, without the need of performing tests at industrial scale.

The assessment of the viability and level of success of a biorefinery alternative depends on the financial, socioeconomic and environmental impact indicators, calculated through different methods. The approach proposed has already been successfully applied to various case studies involving sugarcane biorefineries, such as the evaluation of annexed and autonomous biorefineries [46], integrated and stand-alone second generation ethanol facilities [31], ethanol and n-butanol production [17,19,30,32,33,42,44] and anaerobic digestion of vinasse [47].

2.2. Process description and scenarios definition

A summary description of the five scenarios investigated in this study is shown as follows:

- Scenario 1G2G: production of anhydrous ethanol and surplus electricity in an integrated first and second generation sugarcane biorefinery;
- Scenario ABEW: ABE fermentation with regular microorganism (*Clostridium saccharoperbutylacetonicum* DSM 2152) with a butanol yield of 0.20 g g^{-1} of sugars;
- Scenario ABEM: ABE fermentation with genetically modified strain (*Clostridium beijerinckii* BA101) with improved butanol production of 0.34 g g^{-1} of sugars;
- Scenario ALCD: catalysis of anhydrous ethanol for the production of n-butanol and co-products using [RuCl(η^6-p-cymene)(bis(diphenylphosphanyl)-methane)]Cl catalyst;
- Scenario ALCT: catalysis of anhydrous ethanol for the production on n-butanol and co-products using hydroxyapatite catalyst with Ca/P ratio of 1.67 in six reactors coupled in a series-parallel arrangement.