



## Comparison of energy efficiency and economics of process designs for biobutanol production from sugarcane molasses

A.B. van der Merwe, H. Cheng, J.F. Görgens\*, J.H. Knoetze

Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

### HIGHLIGHTS

- ▶ Conceptual process designs for different process routes of biobutanol production.
- ▶ Fed-batch fermentation with *in situ* gas, LLE and steam stripping distillation.
- ▶ Design 3 with a favorable energy performance (positive NEV and ER larger than one).

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### ABSTRACT

Development of technologies for biobutanol production by fermentation has resulted in higher final butanol concentrations, less fermentation by-products and higher volumetric productivities during fermentation, together with less energy intensive separation and purification techniques. These new technology developments have the potential to provide a production process for butanol from sugarcane molasses that is economically viable in comparison to the petrochemical pathway for butanol production. This objective was investigated by developing process models to compare three different possible process designs for biobutanol production from sugarcane molasses. The first two process routes incorporate well established industrial technologies: Process Route 1 consisted of batch fermentation and steam stripping distillation, while in Process Route 2, some of the distillation columns were replaced with a liquid–liquid extraction column. Some of the best production strains in these process routes, which include *Clostridium Acetobutylicum* PCSIR-10 and *Clostridium Beijerinckii* BA101, can produce total solvent concentrations up to 24 g/L. Process Route 3 incorporated fed-batch fermentation and gas-stripping with CO<sub>2</sub>, an unproven technology on industrial scale. Process modeling in ASPEN PLUS® and economic analyses in ASPEN Icarus® were performed to determine the economic feasibility of these biobutanol production process designs. Process Route 3 proved to be the only profitable design in current economic conditions in South Africa. Improved fermentation strains currently available are not sufficient to attain a profitable process design without implementation of advanced processing techniques. Gas stripping is shown to be the single most effective process step of those evaluated in this study, which can be employed on an industrial scale to improve process economics of biobutanol production.

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### 1. Introduction

*n*-Butanol can be produced from plant biomass (sugar) by fermentation (“biobutanol”) or from fossil fuels (“petrobutanol”); biobutanol and petrobutanol have the same chemical properties. Butanol is primarily used industrially as a solvent or component in surface coatings, and with characteristics similar to petroleum fuel, it is a superior biofuel to ethanol. Biobutanol is more energy dense and less hygroscopic than bioethanol, resulting in higher possible blending ratios with gasoline. It is also less corrosive

and more suitable for distribution through existing pipelines for gasoline than ethanol, and the Reid vapor pressure of butanol is 7.5 times lower than that of ethanol, making it less evaporative/explosive [1].

Although fermentation of carbohydrates to the mixture of butanol with acetone and ethanol (ABE) was a well established process, ABE butanol could not compete on a commercial scale with the latter butanol produced synthetically from petrochemical industry, as cost issues, the relatively low-yield and sluggish fermentations, as well as problems caused by end product inhibition and bacteriophage infections [2]. In 1945, 66% of the total butanol and 10% of the total acetone production in the world were obtained by ABE fermentation, making it the largest scale bioindustry ever run,

\* Corresponding author. Tel.: +27 21 808 3503; fax: +27 21 808 2059.

E-mail address: [jgorgens@sun.ac.za](mailto:jgorgens@sun.ac.za) (J.F. Görgens).

second only to ethanol fermentation [3]. However, as the petrochemical industry evolved during the 1960s, the production of acetone and butanol by fermentation virtually ceased. Today most *n*-butanol is produced chemically from petroleum sources by either the oxo- or adol-processes [2].

During the 1980s and 1990s substantial progress was made in the development of genetic systems for the solventogenic *Clostridia* used in ABE fermentation, which would allow for the development of strains with improved fermentation characteristics [4]. However, the major hurdles to overcome before an economically competitive biological process could be reintroduced were: the high cost of the substrate, the low fermentation product concentration (about 2% because of solvent toxicity to the micro-organism), and the high product recovery cost (distillation has been used in the past). A number of factors presently stimulate the present interest in technology development of biobutanol production. These include the current instability of oil supplies from the Middle East [5], a readily available supply of renewable agriculturally based biomass [6], and the call for reduction of greenhouse gas emissions [7]. Ultimately, a revival of the ABE fermentation process is dependent on favorable economic conditions relative to petrochemical-based processes [8].

During the past decade, a hyper-butanol-producing strain has been developed as a result of the application of modern molecular techniques and genetic manipulation to the solventogenic *Clostridia* [9]. Experimental and computational engineering efforts have also led to improved fermentation techniques, downstream processing, and process integration. All these developments resulted in a significant increase in biobutanol titer, yield and recovery [10]. Computer simulation is used to scale up experimental results and provide meaningful predictions on the performance and economics of a full scale industrial plant. The number of publications available regarding ABE process simulation is however very limited [11–15].

The aim of this study is to develop conceptual process designs to compare different possible process routes for industrial scale biobutanol production from sugarcane molasses in South Africa. These process designs are captured in AspenPlus process models (Aspen Icarus 2006) and each evaluated for economic viability using the IcarusPlus software package (Aspen Plus 2006). Higher oil prices, low feedstock cost (molasses), and improved strains and technology, will facilitate improvement on previous biobutanol production processes, anticipating an economic viable process able to compete with synthetic butanol.

## 2. Improved biobutanol production strains and technologies

Batch fermentation with simple distillation was previously used for industrial butanol production. The strains used produced ABE in the ratio of 3:6:1, with a maximum solvent concentration of 22 g/L, under laboratory conditions. In practice, however, much lower concentrations were achieved [16].

### 2.1. Strains

Table 1 presents the fermentation performance of strains used in this study. Three of the best strains currently available for glucose fermentation were chosen to determine the effect of different solvent concentration, productivity, and ABE ratio (volume) on the design and economics of the butanol production process.

### 2.2. Fermentation

Fed-batch and continuous fermentation have offered substantial improvements in volumetric productivity compared to simple

batch fermentation [4,9,17–20]. However, fed-batch fermentation requires *in situ* product recovery, while for continuous fermentation multiple reactors are required to achieve a reasonable product concentration [4]. Another means to improve the continuous fermentation process is to apply cell recycle or immobilization of cells, but none of these technologies have been implemented on industrial scale [9]. Therefore fed-batch fermentation, reliant on an *in situ* product recovery technique, and repeated batch fermentation, rendering an overall semi-continuous process, was chosen for process modeling.

### 2.3. Product recovery

Product recovery presents one of the challenges associated with the commercial production of biobutanol due to the low concentrations of the product obtained from fermentation, which can lead to large energy consumption during the separation and purification steps. The separation is also complicated due to the homogeneous ethanol–water azeotrope and the heterogeneous water–butanol azeotrope that are formed [21,22]. Membrane-based systems show a high selectivity for solvents, but might suffer from clogging and fouling, and therefore seem to be more suited for use with immobilized cells [3]. For these reasons membrane techniques are unattractive on industrial scale processes. Adsorption using various adsorbents is the technique with the lowest energy requirements, but is also subject to fouling and has a low capacity and selectivity [3]. Gas-stripping is a simple process for solvent recovery from the fermentation broth, similar to steam stripping distillation; it does not suffer from particulate substrates or from clogging or fouling by biomass, although this technique can lead to insufficient recovery of solvents [3,4]. Liquid–liquid extraction (LLE) can be a viable alternative to azeotropic distillation; when properly incorporated into the flowsheet, it may eliminate the need for azeotropic distillation [12]. LLE also has a high selectivity, but emulsions might form rendering the process less suitable [3]. As far as improved product separation for industrial application goes, there is no clear cut best option, but it appears that LLE and gas-stripping may be preferred.

### 2.4. Economics

Investment estimates from different studies show that large sterilisable vessels for fermentation are expensive and have a substantial influence on the investment cost. However, there are other factors that have equal influence on investment cost, e.g. capital cost for product separation, which is of comparable magnitude [23]. Continuous production has a higher productivity than batch operation and may seem economically more viable, but there are additional expenditures involved for not only the installation of dedicated sterilisation equipment, but also to install piping, valves, and other fixtures capable of reliably supporting absolute sterility at all times. Therefore, purely from the investment cost point of view, it is improbable that continuous operation is of great advantage as the requirement for sterility is of critical importance and governs investment in the plant [23]. The choice of downstream processing technique for product separation also does not have a significant influence on the investment cost. Gas-stripping, liquid–liquid extraction, and membrane evaporation equipment require an investment of roughly similar magnitude as traditional distillation columns [23]. Use of low flux, highly selective pervaporation membranes may even require higher investment costs due to large membrane areas required and other operational problems, such as possible capillary blockages and perforation of the membrane, which can cause sterility problems [23]. Therefore, when deciding upon a novel ABE production system the increased

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