Techno-economics of carbon preserving butanol production using a combined fermentative and catalytic approach

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HIGHLIGHTS

- Catalytic conversion of succinic acid to *n*-butanol were evaluated.
- Fed-batch fermentation for *n*-butanol production were evaluated.
- Hybrid production of butanol can improve yields and reduce CO_2 emissions.

ARTICLE INFO

ABSTRACT

This paper presents a novel process for *n*-butanol production which combines a fermentation consuming carbon dioxide (succinic acid fermentation) with subsequent catalytic reduction steps to add hydrogen to form butanol. Process simulations in Aspen Plus have been the basis for the techno-economic analyses performed. The overall economy for the novel process cannot be justified, as production of succinic acid by fermentation is too costly. Though, succinic acid price is expected to drop drastically in a near future. By fully integrating the succinic acid fermentation with the catalytic conversion the need for costly recovery operations could be reduced. The hybrid process would need 22% less raw material than the butanol fermentation at a succinic acid fermentation yield of 0.7 g/g substrate. Additionally, a carbon dioxide fixation of up to 13 ktonnes could be achieved at a plant with an annual butanol production of 10 ktonnes.
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1. Introduction

The International Energy Agency foresees a rapid increase in biofuel demand, in particular for second-generation biofuels, in an energy sector that aims on stabilising atmospheric CO_2 concentration below 450 parts per million (ppm). Constraints in biofuel production volumes are related to the availability of additional land to generate new feedstock, collection of residues and transportation costs. Industries are thus recommended to focus on currently available feedstock sources in the initial stage of development (IEA, 2010). Life cycle analyses performed indicate that lignocellulosic ethanol generates up to 91% less GHG emissions when compared to fossil gasoline or diesel, including the CO_2 released during fermentation (Menon and Rao, 2012). An alternative alcohol

also produced by fermentation is *n*-butanol, hereafter simply butanol. Butanol as fuel replacement to gasoline outcompetes ethanol, biodiesel and hydrogen when its safety and simplicity of use are recognised. It is also compatible in different blends with ethanol and diesel (Menon and Rao, 2012). Conventional butanol fermentation – the ABE (Acetone Butanol Ethanol) process using *Clostridial* cultures pose two main problems restricting industrial production. This include the toxicity of butanol to the culture (maximum concentration tolerable, 10–12 g/l butanol or 20 g/l total ABE), low yield as a considerable amounts of other solvents are produced along with butanol (acetone and ethanol). In addition, acetic and butyric acid are also formed in the process. An obvious solution to inhibition would be to continuously remove the solvents from the broth or to engineer clostridia culture with high tolerance to the fermentation solvents. Recent reports on fermentative bio-butanol production from cellulosic feedstocks have indicated considerable improvements both from yield and solvent recovery

point of views (Ezeji et al., 2004a; Lu et al., 2012; Qureshi et al., 2007; Xue et al., 2013). Several plausible solvent recovery technologies have also been reported in the literature, amongst others gas stripping, pervaporation, liquid–liquid extraction, and adsorption can be listed (Ezeji et al., 2004b; Jin et al., 2011). Of all the techniques, gas stripping has been reported as one of the promising in situ recovery technologies both from operability and economic point of views (Ezeji et al., 2004a; Jin et al., 2011; Lu et al., 2012; van der Merwe et al., 2013; Xue et al., 2013). The fermentation process largely depends on the sugar content of the feedstock, pre-treatment process by which fermentable sugars are liberated, and the *Clostridial* culture used. However, the composition of the product condensate i.e. concentration fractions of acetone, butanol and ethanol to the total ABE is fairly constant regardless of substrate used when gas stripping is employed.

Several national investigations on the future of the chemical industry have pointed out succinic acid (SA) as a cornerstone in future chemical engineering. One of the most interesting properties of the molecule is the potential it has for the production of new polymers, both the acid itself and its derivatives (Bechthold et al., 2008; Zeikus et al., 1999). SA is an intermediate product in the citric acid cycle, but can also be produced as an end-product via anaerobic processes. SA is being promoted as a key compound for the future bio-based chemical industry as it can be converted to several useful chemical compounds (Cheng et al., 2012; Cukalovic and Stevens, 2008; McKinlay et al., 2007; Zeikus et al., 1999). Among the derivatives suggested by several researchers are pyrrolidones which are important solvents, succinate salts which can be used as deicers, γ-butyrolactone (GBL) which is used in the pharmaceutical and agrichemical industry, tetrahydrofurane (THF) which is another important solvent and 1,4-butanediol (BDO) which is a useful intermediary for many processes (Corma et al., 2007; Cukalovic and Stevens, 2008; Delhomme et al., 2009; Paster et al., 2003). The first commercial polymer based on SA derived monomers is the Bionolle (Ichikawa and Mizukoshi, 2012), which is a polyester of SA and BDO, yielding poly(butylene succinate) (PBS). The polymer is yet produced from fossil derived SA, but the production is intended to substitute this with bio-based feedstock in the future. Unlike the conventional ABE fermentation that in addition to butanol also produces CO_2, the SA producing organisms use CO_2 as a feedstock in addition to the carbon source. The loss of carbon has a negative impact on the economics as a significant amount of the raw material is not fully utilized. In this study we explore the possibility to utilize a hybrid butanol production processes that enable conservation of carbon originating from the biomass by the use of a CO_2-fixating fermentation. By this novel hybrid process we circumvent some of the general drawbacks found in the conventional process by utilizing SA fermentation, CO_2 sequestering, following catalytic reduction to add hydrogen to form butanol (Fig. 1). This study provides insights how to further use SA as a key compound in a developing bio-based economy by expanding the portfolio of SA derived products. To end this, a

techno-economic analysis was performed on the conventional biobutanol process, including impact of fermentation holding time based on a low-cost feedstock. The overall economy and performance was further compared to the investigated hybrid process that combines a biochemical and thermochemical process to increase utilization of available biomass.

2. Methods

2.1. Process description

In the scenario studied, butanol fermentation and SA to butanol by the hybrid process was simulated in the Aspen Plus® software. The selected complex dual-phase fermentation used for SA production in *Escherichia coli* with both an aerobic cell growth phase and an anaerobic production phase is difficult to implement in simulations. To cover for different performances and costs to produce SA by fermentation a complementary analysis was made. In both compared processes a biobutanol production of 10,000 tonnes/year was targeted. The pre-treatment and wheat straw hydrolysate (WSH) preparation used as feedstock were not included in the analysis.

2.1.1. Butanol fermentation process

The model initially developed for fermentation of glucose substrate was adapted to handle pentose sugars conversion process. The model was constructed in Aspen Plus®. The model is a steady-state flowsheet model based on a stoichiometric reactor approach. The fermentation stoichiometry is rather a qualitative representation and the yield is controlled according to experimental data (Ezeji et al., 2004b; Mariano et al., 2013). According to the experimental data the fermentation of glucose yields 0.303, 0.155 and 0.007 in g/g-glucose of butanol, acetone and ethanol, respectively. The reactor is assumed to be operated on a fed-batch mode and the conditions are maintained at a temperature of 35 °C and a pressure of 1 atm. The total fermentation time is 200 h and stripping starts after 22 h. In order to render a continuous process, the overall productivity in the model is maintained using average mass flow rates over the total fermentation time. Thus, the mass flow rate of products from the fermenter is 0.556%, (=1/180, the stripping process is operated for 180 h), of the fermentation broth. For the same reason, the substrate intermittently added during the fed-batch fermentation process is simulated as a continuous addition using averaged mass flow rates over the entire fermentation period. Furthermore, the glucose utilization rate is set to 95% and that of pentose sugars is set to 90% (Ezeji et al., 2004b; Mariano et al., 2013).

In the model, the gas stripper is represented by a separator with butanol selectivity set to 20 as a design specification. In addition, no selectivities have been assigned to the butyric and acetic acids since presence of both is not reported in the condensate (Ezeji et al., 2004a). The selectivities for acetone and ethanol are set in
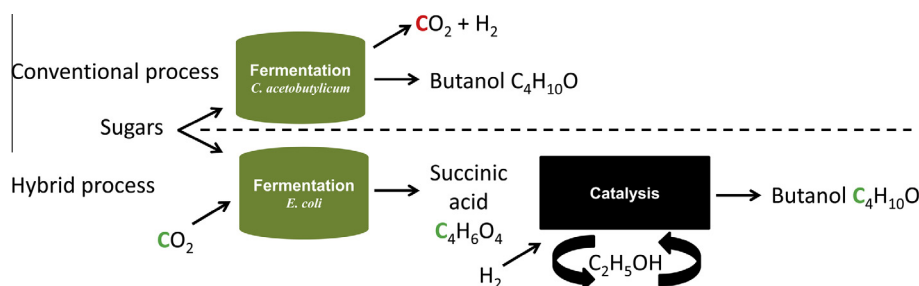

Fig. 1. Overview of conventional and novel hybrid process for butanol production. In the conventional butanol fermentation process CO_2 is released from metabolized sugars. Seen in the hybrid process, CO_2 is fixed during fermentation and the carbon maintained to final product.