



# Fermentative production of butyric acid from wheat straw: Economic evaluation



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## ABSTRACT

The economic feasibility of biochemical conversion of wheat straw to butyric acid was studied in this work. Basic process steps included physicochemical pretreatment, enzymatic hydrolysis and saccharification, fermentation with in-situ acids separation by electrodialysis and product purification. Two scenarios (S1 and S2) were examined assuming a plant with an annual capacity of 10,000 tonnes of product installed in India (due to significantly lower feedstock prices). S1 resulted in a product of 89% butyric acid mixed with acetic acid and S2 produced butyric acid of 99% purity. Unit production cost was estimated at 2.75 and 3.31 \$ per kg product for S1 and S2 respectively. The main part of production cost was attributed to steam for the purification step and electricity for the in-situ acids separation. This unit production cost combined with an estimated butyric acid selling price (year 2014) at 3.50 and 3.95 \$ per kg product (for S1 and S2 respectively) and a plant capacity of 10,000 tonnes indicated an internal rate of return of 14.92% and 12.42% and payback time of 4.28 and 4.70 years for S1 and S2 respectively. Sensitivity analysis showed that under the assumptions of the present study the optimum plant capacity would lie between 10,000 and 15,000 tonnes of product per year.

## 1. Introduction

Butyric acid is a four carbon fatty acid, which is commonly found in milk and milk products such as butter and has diverse applications in food and feed, chemical and pharmaceutical industries (Dwidar et al., 2012). In the chemical industry, the primary application of butyric acid is plastic production (e.g. cellulose-acetate-butyrate) (Cao et al., 2011). Previous research has also shown that butyric acid can be converted to butanol in a two steps fermentation process where sugars are converted to butyric acid in the first step by *C. tyrobutyricum* and in the second (solventogenic) step, butyric acid is converted to butanol by *C. acetobutylicum* (Ramey, 1998). The current annual production of butyric acid is estimated to be around 50,000 t (Sauer et al., 2008) and it is mainly produced by oxidation of butyraldehyde (obtained from propylene derived from crude oil by oxosynthesis). Currently, the chemical synthesis of butyric acid is preferred mainly because of its lower production cost and the availability of the starting materials (Dwidar et al., 2012). Due to the increasing petroleum prices (in the long term), the concerns about greenhouse gas emission and global warming and the customers' preferences, butyric acid production from renewable resources is receiving growing interest from the scientific community and the industry (Zhang et al., 2009; Zigova and Sturdik,

2000). However, biological production of butyric acid (e.g. from lignocellulosic biomasses) is relatively costly (Dwidar et al., 2012) and petroleum based production cannot be economically outcompeted by the renewable alternatives so far.

Wheat straw is the most abundant agricultural biomass in the world after rice straw (Kim and Dale, 2004) with, approximately, 600 million tonnes of wheat straw produced globally in 2009 (estimation based on FAO grain production data) (Bakker et al., 2013). Agricultural biomass is extensively exploited for production of power and biofuels. Particularly, in India, agricultural residues (e.g. rice husk, small wood chips, rice husks, cotton stalks, and other agro-residues) are used for grid power generation but the major portion of agricultural biomass (e.g. straw) is currently left in the fields (Mangaraj and Kulkarni, 2011). However, recent actions encouraged by the governmental policy supporting a low-carbon growth path increased potential exploitation of agricultural biomass (Purohit and Fischer, 2014).

Typical process for biological production of butyric acid from lignocellulosic biomasses such as wheat straw comprises pre-treatment, saccharification, fermentation, extraction and purification. Pre-treatment and enzymatic hydrolysis (saccharification), in general, is similar to 2G ethanol production process (Kazi et al., 2010) with weak acid hydrolysis being one of the most common pretreatment methods also

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for fermentative butyric acid production (Jha et al., 2014). Fermentation and acids extraction processes have been discussed in several review articles where different in-situ extraction strategies including solvent extraction and electrodialysis were suggested (Dwidar et al., 2012; Zhang et al., 2009; Zigova and Sturdik, 2000). Typical solvent extraction methods tested so far include physical extraction, reactive extraction or pertraction using different solvents such as decanol, and alamine 336/oleyl-alcohol with the main disadvantage being their inhibitory effect on the fermentation process. Recently, Baroi et al. (2015a) reported promising results from a butyric acid production method based on the fermentation of pre-treated and enzymatically hydrolyzed wheat straw, which was successfully tested in laboratory as well as in pilot scale. In this method, a single strain (*C. tyrobutyricum*, which cannot hydrolyse cellulose or hemicellulose) fermentation process was applied in combination with in-situ acids separation by Reverse Electro Enhanced Dialysis (REED). This resulted at a high butyric acid productivity, yield and selectivity ( $1.30 \text{ g L}^{-1} \text{ h}^{-1}$ ,  $0.45 \text{ g g}^{-1}$  sugar, and  $0.88 \text{ g g}^{-1}$  acids respectively) which was accompanied by significantly smaller (but not negligible) acetic acid production. One possibility to eliminate acetic acid in the fermentation step is using a co-culture of symbiotic microbial species (methanogens), which are able to convert acetic acid and hydrogen (released by butyric acid producing bacteria) to methane but are not able to consume butyric acid and have similar growth requirements with *C. tyrobutyricum*. This microbial symbiotic relationship is very common and naturally occurs in anaerobic digestion processes (Batstone et al., 2002). Methanogens such as *Methanosarcina* sp and *Methanosaeta* sp. can catabolize  $\text{H}_2\text{-CO}_2$  and acetic acid, respectively (Stams et al., 2003). It is expected that a co-culture of *C. tyrobutyricum* with methanogens will obviously have the advantage of resulting in a fermentation broth containing only butyric acid and (practically) no acetic acid with additional production of methane (which could be used as fuel for the process). On the other hand, the fermentation step will have to be designed for a longer hydraulic retention time in order to avoid washing out of the methanogens, which grow slower than *C. tyrobutyricum* (Khanal, 2008).

To our knowledge, the above mentioned butyric acid efficiency is the highest observed so far in suspended growth fermentation systems and therefore, it is worthy to further examine possibilities for upscaling and commercial exploitation. Techno-economic analysis is a fundamental tool for studying the feasibility of new processes and estimating their economic viability and performance. A representative software package which is commercially available and can be used for simulation and techno-economic analysis of processes is SuperPro Designer<sup>®</sup>. SuperPro Designer<sup>®</sup> has among others been used for the techno-economic analysis of bioethanol production (Kazi et al., 2010; Wooley et al., 2002), bio-diesel production (Marchetti et al., 2008) and biopharmaceutical process optimization (Petrides et al., 2014) by estimating mass and energy balances as well as economic parameters. Furthermore, SuperPro Designer<sup>®</sup> can provide the distribution of cost over different process sections and perform cash flow analysis.

In the present study, a complete plant is envisaged where wheat straw is pretreated, enzymatically hydrolyzed and fermented to butyric acid, which is subsequently separated by applying the process developed by Baroi et al. (2015a). The plant, which is assumed to have a production capacity of around 10,000 t purified acids as main product (MP) from wheat straw, is analyzed and simulated by SuperPro Designer<sup>®</sup>, techno-economic analysis is performed and its economic feasibility is evaluated.

## 2. Methods

### 2.1. Description of the process model

The process model includes five major process steps: feedstock handling, pretreatment, saccharification, fermentation and extraction and purification (see Fig. 1). The detailed process model, developed by

using SuperPro Designer<sup>®</sup> V9.0, is shown in Fig. 2. In addition to the five sections, the model includes heat and power generation units where by-products such as solids and biogas are used for steam and power generation. Feedstock handling includes size reduction, which in combination with pretreatment facilitates the disintegration of the lignocellulosic structure of the biomass and thus increases the release of sugar monomers in the saccharification step. The liquid fraction of the latter step is then used for butyric acid fermentation. Organic acids produced in the fermentation step are extracted by distillation in the final purification step.

In most of the single strain fermentation processes developed so far for butyric acid production acetic acid is a side product even after genetic modification (Zhu et al., 2005). Acetic acid is also produced during the pretreatment. Butyric acid purification technologies after extraction are not yet fully developed and often butyric acid is produced as a mixture (Zigova et al., 1999). Acetic acid (boiling point  $117.95 \text{ }^\circ\text{C}$ ) has an almost similar pKa value as butyric acid (boiling point  $164.85 \text{ }^\circ\text{C}$ ) and both acids form azeotropic mixtures with water making the purification energy demanding. Hence, two scenarios (S1 and S2) were investigated in this study. S1 is based on the fermentation process developed by Baroi et al. (2015a) where a mixture of butyric acid with acetic acid is the main product (MP). S2 is based on the same bacterium used in S1 (*C. tyrobutyricum*) in coculture with methanogens, which are able to convert acetic acid to methane and thus butyric acid is the MP. Each of the scenarios is modelled in SuperPro Designer where materials and energy balances are developed and then used for the economic evaluation of the processes.

#### 2.1.1. Feed stock

Composition, availability and thus prices of wheat straw can vary significantly depending on the climate, soil and harvesting time as well as local market conditions (Molinuevo-Salces et al., 2013). As a result, unit production costs can be affected by these parameters when wheat straw is used as feedstock. In 2009–2010, wheat and rice straw production in India reached 186 million tonnes and 75% of this was either burnt or wasted (Mangaraj and Kulkarni, 2011). Furthermore, prices of wheat straw in India ( $0.0125 \text{ } \$/\text{kg}$  (Mangaraj and Kulkarni, 2011)) are considerably lower than in Denmark and Sweden ( $0.0724 \text{ } \$/\text{kg}$  (Statistik, 2014) and  $0.108 \text{ } \$/\text{kg}$  (Horváth et al., 2013)). Due to large availability and very low prices of straw it is assumed that the plant for butyric acid production from wheat straw considered in the present study will be located in India. Hence, this study considers India as a potential ground for this process.

Major constituents of wheat straw are cellulose, hemicellulose and lignin as shown in Table 1. Furthermore, wheat straw contains silica as 13%–18% of ash content (Antongiovanni and Sargentini, 1991; Halvarsson et al., 2010) and 8–14% water (Bauer et al., 2009; Larsen et al., 2012). The chemical composition of wheat straw used in this study was assumed to be cellulose 39.7%, hemicellulose 23.9%, lignin 20.5% and ash 5.7% as averages of the respective values presented in Table 1.

#### 2.1.2. Feedstock handling and pre-treatment

Feedstock handling includes wheat straw washing and size reduction. Fresh water requirement in this process is assumed to be minimal since water generated in downstream purification steps is used in the washing step. Washed straw is passed through a grinder for size reduction down to 2–3 mm increasing the surface area, which facilitates the subsequent physicochemical pre-treatment step (Njoku et al., 2012). Storage cost is not taken into account for the estimation of unit production cost in this study.

The primary objective of the pretreatment is to make the carbohydrates, imbedded in lignocellulosic biomass, accessible for enzymatic hydrolysis (saccharification) (Galbe and Zacchi, 2002; Taherzadeh and Karimi, 2008). In the process considered in the present study, washed and grinded straw is transferred to the pretreatment reactor where it

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