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Optimal design of an efficient, profitable and sustainable biorefinery producing acetone, butanol and ethanol: Influence of the *in-situ* separation on the purification structure

Ségolène Belletante, Ludovic Montastruc*, Stéphane Negny, Serge Domenech

Université de Toulouse, Laboratoire de Génie Chimique UMR CNRS/INPT/UPS 5503, Toulouse, France

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ABSTRACT

The bio-based *n*-butanol has major potential to replace fossil-based products due to, on the first hand, the decline of crude oil and, on the other hand, since the butanol has high potential as fuel. To set its production in industrial scale the development of tools designing the process is needed. In our work, we focus on second generation biorefinery using wood as feedstock. The biorefinery was composed by the pretreatment, the hydrolysis, the fermentation, the butanol recovery and the purification. The proposed methodology is a multiscale decision support tool for the selection of the optimal process design of the biorefinery producing biobutanol. The optimal biorefinery is selected from the superstructure recapping all feasible scenarios after process modelling and simulation, economic and environmental evaluations and energy integration. Thus, the optimal process is profitable, efficient and sustainable. Moreover, to identify the influence of the biobutanol recovery on the fermentation's performances, the process modelling includes the retroaction of biobutanol recovery. In this study, three biobutanol recovery and four purification scenarios are combined and then processes are compared to select the optimal biorefinery for the bio based butanol production.

1. Introduction

Among biofuel possibilities, bioethanol was the most studied and produced because of its ease of conversion at industrial scale. However butanol has also a high potential as biofuel because of its relevant, favorable physico-chemical properties [1], which are very similar to fuel's ones, as illustrated on Table 1.

Then, any fuel-butanol blended up to a 100% butanol can be utilized in fuel engines without modification of technology [4] and, butanol has also higher energy content than ethanol. Furthermore, butanol has other utilizations [5]: solvent in paints and coatings, chemical building block for the production of several products like polymers such as polypropylene, 1-butene, and intermediate for the production of more complex molecules. As a consequence, in the context of bio-based economy development, it is interesting to produce butanol from renewable resources, and more particularly from biomass.

Historically, from the early twentieth century *n*-butanol was produced *via* the acetone-butanol-ethanol (ABE) fermentation with bacteria such as *Clostridium* type. According to the study of Niemistö et al. [6], the industrial production started at around 1920. However, as soon as the petrochemical production was developed, ABE fermentation was forsaken. Interest in the bio-based butanol only reappeared in the 2000s due to the awareness of the issues of global warming and climate change, but mainly due to the need of alternatives to fossil-based butanol because of the decline of petroleum resources. Currently, many researches focus on the ABE fermentation in many different topics (see Section 2): the genetic engineering to describe new pathways or genetic modifications in order to improve productivity of microorganisms, the bioprocess to elaborate new processes to improve performances of fermentation, etc. However, very few research studies focus on the global process of biorefinery and especially on the biobutanol production [7–9]. Indeed, the industrial development of bio-based butanol needs the thorough study of potential processes to ascertain the economic and ecological viability of these biorefineries. Actually, there are many processes for the production of butanol depending on the feedstock, and in our case we use the ABE fermentation. It consists in the conversion of renewable carbon-based raw materials into bioproducts through a sequence of thermal, physical, chemical and biological steps. Nowadays, three generations of biorefinery were identified according to the feedstocks used [10,11]: the first generation converts starches e.g. corn and sugars beets, the sec-

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* Corresponding author at: Université de Toulouse, Laboratoire de Génie Chimique UMR CNRS/INPT/UPS 5503, 4 Allée Emile Monso, CS 84264, Toulouse 31 432, France.
E-mail address: ludovic.montastruc@ensiacet.fr (L. Montastruc).

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Table 1
Comparison between physic-chemical properties of diesel fuel, gasoline, ethanol and *n*-butanol [2,3].

Properties	*n*-Butanol	Ethanol	Gasoline	Diesel fuel
Lower caloric value (MJ/L)	29.2	21.2	32.5	39
Cetane number	25	8	///	50
Heat of vaporization (MJ/kg)	0.43	0.92	0.36	0.25
Research octane number	96	129	91–99	///
Motor octane number	78	102	81–89	///
Air-fuel ratio	11.2	9	14.6	15
Solubility in water	Immiscible	Miscible	Immiscible	Immiscible

ond generation focuses on lignocellulosic feedstocks like wood and the third generation uses algae. These biomasses can come from agriculture, industrial and households wastes or forestry. In this study, we will focus on the production of bio-based butanol *via* the transformation of wood, because of its world wide availability and the large amount of woody wastes rejected in paper industry. Thus, the reuse of these wastes as raw materials allows creating a circular economy and limiting the natural resources exploitation.

Furthermore, a huge amount of laboratory data about the biobutanol production exists but to create real biorefineries, it is necessary to find methods to reconcile laboratory and the industrial scale. In this way, the methodologies combining process optimization and process design have a high potential. Their function consists in establishing process alternatives, the verification of feasibility, the generation of knowledge on the structural model (topology of the process) and the behavioral model (operating parameters) and finally the determination of the optimal process design and process parameters in order to improve profitability while respecting the desired production quantity, the required quality of product, etc. Various researches [12–16] proposed optimization tools for the process design at various scales of study, for example, method and tools at the supply chain level focus on macroscopic topics like the spatial and time-related aspects, the LCA (Life Cycle Analysis) of the process, network of biorefineries, logistic and variations in markets.

Concerning the biorefinery scale, and more especially the four steps that compose a biorefinery (pretreatment and hydrolysis of feedstock, fermentation, separation or butanol recovery and purification) a two-stages approach for the synthesis and the optimization of biorefineries configuration was proposed by Pham and El-Halwagi [17]: the first step established the potential final bioproducts through possible pathways from several fixed feedstock, and then the second step optimized the process in function on the economic and process performances of the biorefinery. Nevertheless, this method focus on the conversion pathway, consequently the pretreatments, the separations and the purifications are not considered. The optimization model of Moncada et al. [18] established the biorefinery's optimal configuration with respect to the economic, environmental and technical objectives to produce biochemical products and bioenergy. The different biochemical pathways are simulated to obtain accurate mass and energy balances and then compared, but the entire process is not studied. We underline that the model is applied for a specific geographic area with the aim to include the local economic policy of a country. Sammons Jr. et al. [19] focused on the maximization of the Net Present Value (NPV) and the minimization of the ecological impact through empiric calculations. This model includes energy integration (Pinch method) and the use of green solvents in the process. To simplify the calculation, they created a library of processes based on experimental data and process simulation. Zondervan et al. [20] proposed a black box model determining the optimal multiproduct biorefinery from a superstructure. Their Mixed Integer Nonlinear Programming (MINLP) model minimizes costs, maximizes yields and minimizes wastes in order to determine the optimal pathway for each bioproduct. Moreover, it calculates the optimal allocation of several feedstocks for each pathway. However, the calculation of separations is based on separation factors, thus the influence of the thermodynamic is not modeled. Geraili et al. [21] proposed a tool based on the superstructure of a multiproduct biorefinery. Their Linear Programming model determined the optimal process after process simulation with complex kinetics and some optimizations of operating conditions. The objectives are mainly the maximization of the production and the NPV, therefore either environmental criterion or energy integration are considered.

Some researches focus on the integrated biorefinery, and more especially on the integration of energy or water networks, two of the most important operating costs in a biorefinery. The work of Grossmann and Martín [22] aimed to the minimization of energy and water consumptions in first and second generation of biorefinery producing bioethanol. They proposed a two-steps model which minimalizes energy consumption by designing the biorefinery from a superstructure with a MINLP model, and then optimizes water network to minimize freshwater. They proposed a very complete superstructure which encompasses the new technological breakthrough in the domain.

Nevertheless, in addition to the energy consumption, the separation step is another preponderant issue for the production of biobutanol because the fermentation and the separation are coupled in order to improve the fermentation performances. Therefore, the combination of fermentation and separation must represent a large part of the analysis. Some researches interested to this issue. For example, Zondervan et al. [20] studied biorefinery alternatives for the production of ethanol, butanol, acetone and succinic

Table 2
Characteristics of Clostridia bacteria.

Bacterium	*C. acetobutylicum*	*C. beijerinckii*	*C. saccharobutylicum*	*C. saccharoperbutylacetonicum*
Studied range of temperature (°C)	30–37	30–37	35–37	30
Studied range of pH	4.3–6.5	4.7–6.5	4.5–6.5	5.5–6.5
Dilution rate (h^{-1})	0.287	0.07	0.13	0.20
ABE Productivity (g/(L h))	2.08	0.58	0.85	1.85
Acids productivity (g/(L h))	0.861	0.175	0.13	N/A
ABE Concentration (g/L)	7.25	8.29	7.74	9.27
Acids Concentration (g/L)	3.0	2.5	1.17	N/A
Consummed substrates	Glucose, xylose, arabinose, mannose, cellobiose, galactose, starch, lactose, sucrose, fructose, lactose, maltose	Glucose, xylose, arabinose, cellobiose, mannose, galactose, starch, sucrose, fructose, maltodextrin, sorbitol, mannitol	Glucose, xylose, arabinose, cellobiose, mannose, galactose	Glucose, starch, maltose, molasses
References	[28–31]	[31–34]	[31,34,35]	[31,36,37]

N/A: no information.