CHEMICAL ENGINEERING TRANSACTIONS

VOL. 86, 2021

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6 **ISSN** 2283-9216

DOI: 10.3303/CET2186171

Safety and Control Analysis of Hybrid Liquid-Liquid Extraction and Divided Wall Column for Biobutanol Purification

Juan Gabriel Segovia-Hernandez[a,*], Eduardo Sánchez-Ramírez[a], Ernesto Flores-Cordero[b], Juan José Quíroz-Ramírez[a], Massimiliano Errico[c]

[a] Universidad de Guanajuato, Departamento de Ingeniería Química, Noria Alta S/N; C.P. 36050; Guanajuato, Gto.
[b] Universidad de Guanajuato, Departamento de Ingeniería en Biotecnología, Av. Ing. Javier Barros Sierra #201 esq. Av. Baja California; Ejido Santa María del Refugio; Celaya, Gto.; C.P. 38110
[c] Department of Green Technology, Faculty of Engineering, University of Southern Denmark. Campusvej 55, 5230 Odense M, Denmark
gsegovia@ugto.mx

Butanol is getting attention among the possible biofuels as an alternative to bioethanol. Compared to bioethanol, biobutanol shows less miscibility with water, less flammability and corrosivity, and it has the advantage of being able to directly replace gasoline in the car engines without any modifications. However, the production cost from the Acetone-Butanol-Ethanol (ABE) fermentation process remains high, mainly due to the low yield of butanol. The conventional recovery of butanol by distillation is a process of high energy consumption that has greatly restricted its industrial production. In this work different hybrid configurations, based on liquid-liquid extraction and dividing wall columns were examined. Sustainability was analysed based on green metrics, inherent security, and control properties through open and closed-loop policy using PI controllers. The results indicate that as long as the process is highly intensified, the sustainability and the inherent safety are improved but not necessarily the control properties. The best alternative was selected as a compromise between contrasting objective functions.

1. Introduction

The increase in crude oil price and the dependence on non-renewable sources has generated a great interest in the sustainable production of biofuels through the fermentation of residual biomasses. Butanol is one of those fuels that can be produced from agricultural crops such as corn and molasses using *Clostridium acetobutylicum* or *C. beijerinckii*. Unlike ethanol and other fuels obtained by fermentation, butanol has some interesting properties: a) its energy content is 30% higher than ethanol; b) its low vapor pressure facilitates its application in existing gasoline pipelines; c) it is not sensitive to water; d) it is less volatile; e) it is less toxic; f) it is less flammable, and g) can be mixed with gasoline in any proportion. The development of the ABE process reached its peak during World War II since it was used for the acetone production and it was easily forgotten during the development of cheap oil-derived alternatives. Lately, it was observed a renewed interest in the ABE fermentation process due to the achievements reached in fermentation technologies (Patrascu et al. 2017). However, the yield in the production of butanol from biomass is low, making its production by fermentation uneconomical. Processing diluted effluents has the consequence of energy intensive separation and purification steps, accounting approximately for 60-80% of the total annual costs. In this regard, taking advantage of the principles of process intensification, a combination of liquid-liquid extraction and advanced distillation technologies could be used to increase the concentration of the diluted stream and then purify the main product. In this context, Errico et al. (2016) and Sanchez-Ramirez et al. (2018) have analysed and compared different possible processes for the purification of butanol based on conventional distillation and hybrid distillation systems. The results indicated that the combination of liquid-liquid extraction and distillation represents a cost-effective design alternative. Among different intensified distillation alternatives, the dividing wall column (DWC) was proved to be a promising solution for separating and purifying the effluents produced by fermentation (Errico et al., 2017). The control of different process alternatives for the ABE process was

Paper Received: 30 October 2020; Revised: 16 February 2021; Accepted: 4 May 2021
Please cite this article as: Segovia-Hernandez J.G., Sanchez-Ramirez E., Flores-Cordero E., Quiroz J., Errico M., 2021, Safety and Control Analysis of Hybrid Liquid-liquid Extraction and Divided Wall Column for Biobutanol Purification, Chemical Engineering Transactions, 86, 1021-1026 DOI:10.3303/CET2186171

considered by Sanchez-Ramirez et al. (2017) using both open-loop and closed-loop analysis and proving the controllability of hybrid systems. The current and future objectives of process engineering are not only to maintain and reduce the cost of the products, but also to simultaneously reduce the impact on the environment and human health. The growing concern for the environment, the increase of strict standards for the release of chemicals into the environment and economic competitiveness have led to more environmentally friendly approaches that have resulted in pollution prevention through the waste reduction and the efficiency maximization (Constable et al., 2002). Green process engineering is an important tool that could make significant contributions in driving the process sustainability to the benefit of the economy, the environment and society. Some examples of current and future applications of ecological process engineering have been presented, particularly in the areas of biofuels (Jiménez-González et al., 2012). Nevertheless, no study explored the sustainability and inherent safety of the acetone, butanol, ethanol purification based on the combination of liquid-liquid extraction and DWC. In this paper the configurations proposed by Errico et al. (2017) were reconsidered to analyse their sustainability, based on the green metrics proposed by Jiménez-González et al. (2012), and their inherent safety. The analysis is complemented with the study of open loop control properties using the technique of singular value decomposition.

2. Case Study

Errico et al. (2017) presented a complete synthesis methodology to generate separation alternatives to purify biobutanol. In brief, the methodology starts from a hybrid process designed with a liquid-liquid extractive column and a set of three conventional distillation columns. Considering this reference case, Errico et al., (2017) applied a systematic methodology to produce several alternatives, liquid−liquid extraction-assisted conventional DWC configurations and liquid−liquid extraction-assisted nonconventional DWC configurations. All the alternatives were designed considering the NRTL-HOC as thermodynamic method to model the interactions among components. This method is recommended for polar, nonpolar, and associating compounds. It takes into account solvation effects and strong association. The characteristics of feed stream considered is presented in Table 1. The synthesis methodology was based on the inclusion of thermal couplings and both movement and elimination of column sections. All the alternatives generated were evaluated and optimized by means of a differential evolution with tabu list optimization algorithm, evaluating the total annual cost and the eco-indicator 99 as economic and environmental performance indexes respectively. In this work, the ten hybrid designs reported in Figures 1 and 2 have been considered and evaluated under different indexes.

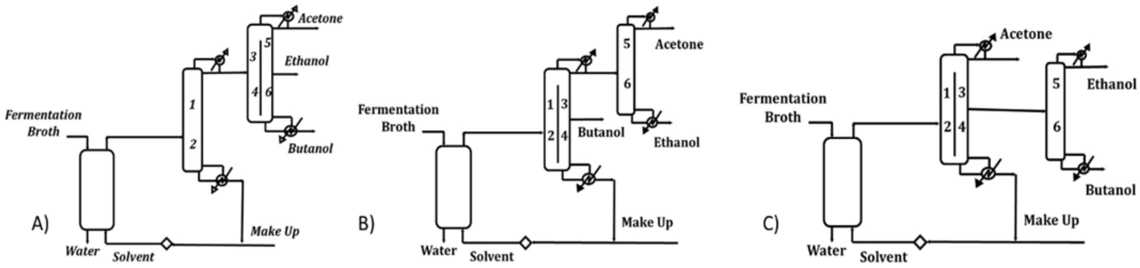

Figure 1: Liquid−liquid extraction-assisted conventional DWC configurations

Table 1: Feed characterization

Temperature (K)	322.04
Vapor Fraction	0
Flowrate (kg h-1)	45.35
Composition (wt %)	
Butanol	0.3018
Acetone	0.1695
Ethanol	0.0073
Water	0.5214

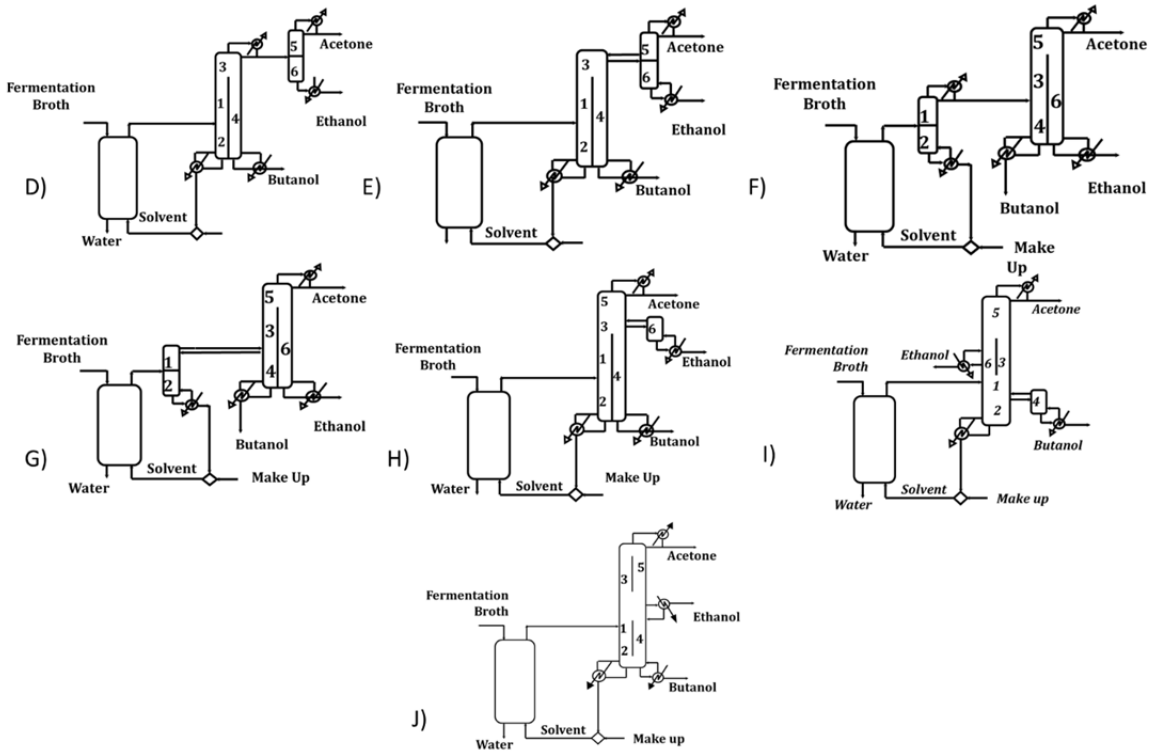

Figure 2: Liquid−liquid extraction-assisted nonconventional DWC configurations

3. Process Risk Quantification, Green Process Evaluation and Control Dynamic Test

To compare the selected configurations, the current analysis was conducted in three parts: the process risk quantification, the green process evaluation, and finally, the control properties test.

Initially, the risk quantification was evaluated by means of the individual risk (IR). The IR is defined as the risk of injury or decease of a person in the vicinity of a hazard (Freeman, 1990). The mathematical expression for calculating the individual risk is the following:

$$IR = \sum f_i P_{x,y} \tag{1}$$

Where *fi* is the occurrence frequency of incident i, whereas $P_{x,y}$ is the probability of injury or decease caused by the incident i.

Considering the background presented by Jiménez-González et al. (2012), in this work three green indexes have been considered to evaluate the alternatives in Figures 1 and 2, the mass intensity (MI), the E-factor and the greenhouse gas emission. The mass intensity is the total amount of mass required to produce a unit of product or service, usually on a wt/wt basis. The mass intensity is defined as follows:

$$MI = \frac{Total\ mass\ used\ in\ a\ process\ step\ (kg)}{Mass\ of\ product\ (kg)} \tag{2}$$

The E-factor is the mass ratio of waste to desired product.

$$E - factor = \frac{Total\ waste\ (kg)}{kg\ product} \tag{3}$$

The E-factor is the amount of waste produced in the process, defined as everything but the desired product respect to the amount of product.

Another metric to evaluate the greenness of a process is the greenhouse emissions. Reducing CO_2 emissions is an absolute necessity for the chemical process industries in order to meet the environmental targets of many international agreements. The CO_2 emission is calculated as follow:

$$[\mathrm{CO_2}] = \left(\frac{\mathrm{Q_{fuel}}}{\mathrm{NHV}}\right)\left(\frac{\mathrm{C\%}}{100}\right)\alpha \tag{4}$$

Where α = 3.67 is the ratio of molar masses of CO_2 and C, while NHV (kJ/kg) represents the net heating value of a fuel with a carbon content of C %. In this work, it is assumed that all energy involved in ABE purification comes from burning CH_4 gas.
As a complement to this study, the control properties were analyzed for all configurations using the singular value decomposition technique (SVD). Let A be an *m* × *n* real matrix of rank *r*. Then there exist orthogonal matrices U ∈ $\boldsymbol{R}^{m\times m}$, V ∈ $\boldsymbol{R}^{n\times n}$ and a diagonal matrix Σ ∈ $\boldsymbol{R}^{m\times n}$ with nonnegative diagonal entries $\sigma_1, \sigma_2, ..., \sigma_n$; such that:

$$G = V \sum W^H \quad (5)$$

where $\Sigma = \mathrm{diag}\,(\sigma_1, \sigma_2, ..., \sigma_n)$, σ_i = singular value of $\Sigma = (\lambda_i)^{1/2}(GG^H)$; $V = (v_1, v_2, ..., v_n)$, matrix of the left singular vectors, and $W=(w_1, w_2, ..., w_n)$, the matrix of right singular vectors. The interpretation is: linear mapping y=Ax can be decomposed as a) compute coefficients of x along with input directions w_i; b) scale coefficients by v_i; c) reconstitute along output directions σ_I (Luyben, 2008). To generate G for all configurations, first, open-loop dynamic responses to changes in the manipulated variables (in this work 1% of the nominal value) around the assumed operating point were obtained. For this case study manipulated variables are reflux ratio, reboiler duty and flowrate side stream and the control variables are each composition in output stream. The responses were obtained using Aspen Dynamics. Finally, a closed-loop test was performed using a PI controller, using LV configuration, and the integral of the absolute error (IAE) as performance criteria. Since butanol is the component of interest, only this component was considered for this controllability study in two schemes: initial scheme (Figure 1A) and most intensified scheme (Figure 3J). The tuning parameters are reported in Table 2.

4. Results

In this section, the obtained results will be shown along with a brief discussion. Starting with the controllability analysis, step changes in the input variables were implemented and the open-loop dynamic responses were registered. Figure 3 presents the minimum singular value and condition number for some representative schemes of this study. Configurations of Figure 1A and Figure 2G have the highest value of σ*. The results indicate that configurations that present a thermal coupling in top or bottom or a DWC as last unit, show better dynamic behaviour.

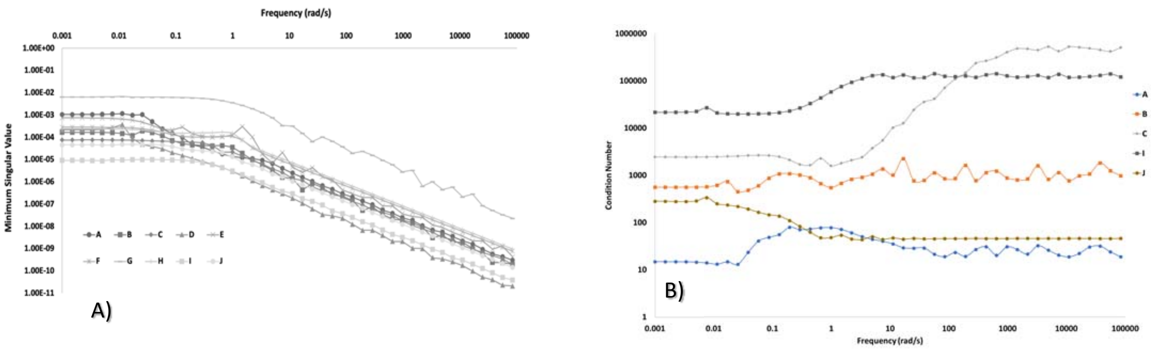

Figure 3. Minimum Singular Values (A), and Condition Number (B)

At low frequencies configurations of Figure 1A, and Figure 2J showed the lowest condition number and highest minimum singular value. These results indicate that arrangements with only one interconnecting thermal linking or thermal links in side stream will present worst control properties. From a physical point of view, low values of the minimum singular value and high values of the condition number imply large movements in the control valves for changes in the set points and load rejection. It is apparent that the presence of recycle streams, instead of deteriorating the dynamic behavior of separation sequences, may contribute positively to their dynamic properties. The control properties study showed marked trends regarding the thermal couplings. A reduction in the number of interconnections in intensified separation systems does not necessarily provide the operational advantages originally expected given the resulting simpler structural design. However, the scheme with the highest level of intensification (Figure 2J), even though at low frequencies presents relatively good dynamic behavior, is not actually the best one. Regarding safety analysis evaluated by the IR, an initial correlation is found. Observing those schemes named conventional DWC columns (Figure 2), it would be logic at first sight to presume that the safer scheme is associated to the lower heat duty or the to the lower operative pressure. However, considering the results shown in Table 3 it would seems contradictory since the configuration of Figure 1B (with higher reboiler heat duty) is indeed the safer one of those reported in Figure 1. Note, the closed loop analysis shows a similar behavior than the open-loop analysis. The scheme of Figure 1A show the lowest IAE value in this study.

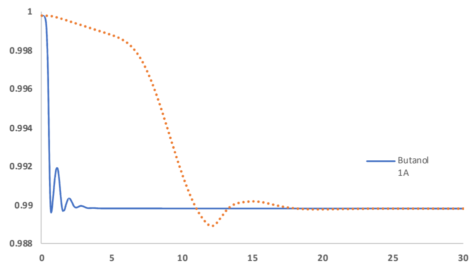

Figure 4. Closed-loop analysis for butanol

Table 2. Tunning results for the closed-loop analysis

Scheme	Ti	Kc	IAE
A	35	115	0.00595615
J	115	250	0.0829786

Table 3. Performances Indexes for the cases of study

Performance Indexes	Figure 1a	Figure 1b	Figure 1c	Figure 2d	Figure 2e	Fig2f	Figure 2g	Figure2h	Figure2i	Figure 2j
TAC [k$ yr^{-1}]	111.86	122.99	128.45	108.54	105.57	115.5	101.78	100.85	100.59	97.88
EI99 [kpoints yr^{-1}]	17.5	19.5	16.74	13.73	12.93	14.34	13.3	12.79	14.74	12.22
IR*10^4 (Prob./y)	5.04	2.56	5.04	2.56	5.04	2.56	5.04	5.04	5.04	2.52
CO_2 [Ton/h]	0.458	0.614	0.490	0.405	0.385	0.378	0.397	0.427	0.393	0.352
E factor [kg/kg]	8.024	8.021	8.021	8.020	8.034	8.023	8.024	8.023	8.065	8.026
MI [kg/kg]	1.003	1.001	1.001	1.000	1.009	1.003	1.003	1.003	1.030	1.004

Note that in Table 3, the schemes with the lowest IR values are associated to the configurations of Figure 1B and Figure 2D and 2J. These configurations have the common feature of separating the mixture acetone-ethanol in a single conventional column. These two components are those in the lowest amount resulting in a lower IR index. This is true also for the configurations of Figure 2F and 2J since they realize the separation of the three products in a single equipment. Regarding the green metrics, greenhouse gas emissions, E factor, and MI, according to Table 3, the complete set of the ten schemes considered seems to have a relatively good behavior. A main correlation on decreasing CO_2 emissions with the intensification of the process can be observed. On the other hand, the E factor presents values near to the values presented for bulk chemicals, all cases the E factor is almost 8 and the bulk chemicals is 5. The mass intensity values for all cases of study were almost 1. It is interesting how these values are related with the recovery restriction fixed on the optimization procedure as minimal recoveries. Table 3 shows the main design parameters for the schemes of Figure 2I and 2J.

Table 4. Design parameters for scheme of Figure 2I and 2J

	Figure 2I	Column section				Figure 2J	Column section		
	Extractor	1+2	4	3+5	6	1+2	4	5+3	6
Number of stages	5	43	26	71	7	43	43	71	7
Feed location	-	13	-	-	-	13	.	-	-
Reflux ratio	-	-	-	-	-	-	-	0.644	-
Distillate [kg/h^{-1}]	-	-	-	7.716	-	-	-	7.717	-
Residue [kg/h^{-1}]	-	712.159	13.681	-	0.317	712.108	13.681	-	0.316
Liquid split [kg/h^{-1}]	-	43.460	17.383	-	0.420	43.463	17.383	-	-
Extract [kg/h^{-1}]	733.873	-	-	-	-	-	-	-	-
Solvent [kg/h^{-1}]	712.147	-	-	-	-	-	-	-	-
Reboiler duty [kW]	-	69.920	0.633	-	0.022	69.920	0.633	-	0.023

5. Conclusions

In this work, the inherent risk, the green process evaluation and the control properties were tested to a set of 10 hybrid designs. A previous work (Errico et al., 2017) reported a reduction of about 22 % of the TAC and 18 % of an environmental index for the alternatives with the highest level of intensification (Fig 2I and 2J). In this work, it was observed that the inherent risk is lower in configurations where acetone-ethanol are separated in a single column. This is due to the fact that the pair acetone-ethanol represents the lowest amount present in the fermentation broth. In brief, to perform this separation in a single column reduce the IR value about 50% compared to the other configurations examined. According to the green metrics results, as long as the intensification level increases, the energy consumption and the CO_2 emissions are reduced. Moreover, the complete set of separation alternatives showed relatively good values of E-factor and Mass Intensity in comparison with current chemical industries. In general terms, the scheme with a high level of intensification showed relatively good dynamic properties at low frequencies. However, the scheme with the highest level of intensification (scheme of Figure 2J), even though at low frequencies presents relatively good dynamic behaviour, is not actually the best one. In other words, as long as the high level of intensification is reached, not always the best dynamic properties may be obtained, a similar conclusion is obtained in the application of intensification techniques applied to ethanol purification. Nevertheless, the configuration of Figure 2J is competitive regarding IR, green metrics, and dynamic properties in comparison with the other alternatives.

Acknowledgments

Financial support provided by the Universidad de Guanajuato and CONACyT (México) is gratefully acknowledged. ME acknowledges the funding received from the European Union’s Horizon 2020 research and innovation programme under Marie Skłodowska-Curie grant agreement No 778168.

References

Constable D.J.C., Curzons A.D., Cunningham V.L., 2002, Metrics to “green” chemistry - Which are the best? Green Chem. 4, 521–527.

Errico M., Sanchez-Ramirez E., Quiroz-Ramirez J.J., Segovia-Hernandez, J.G., Rong, B.-G., 2016, Synthesis and design of new hybrid configurations for biobutanol purification, Computers and Chemical Engineering, 84, 482-492.

Errico M., Sanchez-Ramirez E., Quiroz-Ramirez J.J., Rong, B.-G., Segovia-Hernandez, J.G., 2016, Multiobjective optimal acetone-butanol-ethanol separation system using liquid-liquid extraction-assisted divided wall columns, Industrial and Engineering Chemistry Research, 56, 11575-11583.

Freeman R.A., 1990, CCPS guidelines for chemical process quantitative risk analysis. Plant/Operations Prog. 9, 231–235.

Luyben W.L., 2008, Control of the Heterogeneous Azeotropic n -Butanol / Water Distillation System Energy Fuels, 22, 4249–4258.

Jiménez-González C., Constable D.J.C., Ponder C.S., 2012, Evaluating the “greenness” of chemical processes and products in the pharmaceutical industry - A green metrics primer, Chem. Soc. Rev. 41, 1485–1498.

Patrascu I., Bildea C.S., Kiss A.A., 2017, Eco-efficient butanol separation in the ABE fermentation process, Separation and Purification Technology, 177, 49-61.

Sanchez-Ramirez E., Alcocer-Garcia H., Quiroz-Ramirez J.J., Ramirez-Marquez C., Segovia-Hernandez J.G., Hernandez S., Errico M., Castro-Montoya A.J., 2017, Control properties of hybrid distillation processes for the separation of biobutanol, Journal of Chemical Technology and Biotechnology, 92, 959-970.

Sanchez-Ramirez E., Quiroz-Ramirez J.J., Segovia-Hernandez J.G., Errico M., 2018, Biobutanol purification by liquid-liquid extraction assisted divided wall columns, Chemical Engineering Transactions, 69, 217-222.