

Economic and environmental optimization of the biobutanol purification process

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Abstract Current technologies for the production of biobutanol by fermentation have improved the production processes. These new technology improvements are economically viable with respect to the petrochemical pathway. For this, the aim of this paper is to compare four different process designs for the purification of biobutanol by solving a multi-objective optimization process involving two objective functions: the total annual cost and return of investment as economic functions and the associated eco-indicator 99 as an environmental function. The process associated to the routes A, B, and C consists of a steam stripping distillation and distillation columns, while the process D includes distillation columns with a liquid–liquid extraction column. Process modeling was performed in the Aspen Plus software, and the multi-objective optimization was conducted using differential evolution with tabu list as a stochastic optimization method. Results indicate that the process route D is the most profitable design and the process route C has the lowest environmental impact measured through the eco-indicator 99 method. Additionally, the use of a solar collector against steam has been compared in order to produce the required heat duty needed in every single distillation column to have a broader view about the environmental and economic impact of these devices.

Keywords Biobutanol separation · Economic and environmental optimization · Differential evolution with tabu list · Biofuels · Solar collector

List of symbols

ABE	Acetone–butanol–ethanol
C_{TM}	Capital cost of the plant
C_{ut}	Utility costs
DDE	Dynamic data exchange
DE	Differential evolution
DETL	Differential evolution with tabu list
D_{cn}	Column diameter
ETSC	Evacuated tube solar collector
F_m	Distillate fluxes
GAs	Genetic algorithms
LLE	Liquid–liquid extraction
LCA	Life-cycle assessment
N_{tn}	Total column stages
N_{fn}	Feed stages
ROI	Return of investment
RFS	Renewable fuel standard program
R_m	Reflux ratio
TAC	Total annual cost
TL	Tabu list
x_m	Vectors of required purities
y_m	Vectors of obtained purities

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Introduction

During the last decades, there has been an increasing interest for renewable energy sources because of the problems associated to global warming, climate change, and volatile oil supply (Brekke 2007). Further environmental

concerns have resulted in governmental actions in order to establish a significant energy independence and to promote environmental friendly fuels (Ezeji et al. 2004). In addition, several researches are focused on decreasing the CO₂ emissions and the reduction of the dependency on fossil fuels, especially oil, due to environmental as well as geopolitical reasons (Wenzel 2009; Bulatov and Klemes 2009). Nowadays, there are several biofuels that can be produced from biomass through fermentation of lignocellulose such as ethanol and biobutanol (Chouinard-Dussault et al. 2011; Ezeji et al. 2007). Although ethanol is currently the most used biofuel, several properties of butanol, such as higher energy density, lower steam pressure, less flammability, and hydrophobicity are leading to a growing interest in biobutanol over bioethanol (Ezeji et al. 2007). Particularly, in the industry, there is an intensive interest in the use of biobutanol. In 2007, Green Biologist Ltd reported a patented hydrolysis technology to be integrated into the biofuel fermentation process to reduce the feedstock and manufacturing cost. Butanol is used as solvent, hydraulic fluid, detergent, antibiotic, etc. (Brekke 2007); however, it may also be used as fuel. Currently, butanol is mainly produced via chemical synthesis through the oxo process, but butanol can also be produced via fermentation.

The first report about biobutanol produced in the microbial fermentation was reported by Louis Pasteur in 1861 (Brekke 2007). Several species of *Clostridium* bacteria are capable of metabolizing different sugars, amino and organic acids, polyalcohols, and other organic compounds to butanol and other solvents (Al-Shorgani et al. 2012). Butanol, being of relatively high value, is usually the most desired product. However, the main disadvantage of biobutanol is its low production, which conducted to choose ethanol as alternative biofuel over butanol during the oil crisis in 1970s and 1980s. Nevertheless and despite the inhibition effects in fermentations, important improvements are reported to increase tolerance level of butanol, explaining the increasing studies about it in recent years. Moreover, a limited attention has been paid to the distillation process in the production of acetone/ethanol/biobutanol and its optimization. In the distillation process, the energy employed and the efficiency can be greatly influenced by the water and biobutanol content in the overhead distillate of the biobutanol column (Delgado-Delgado et al. 2015; Emtir and Etoumi 2008) (see Fig. 1). Therefore, the reduction of water and biobutanol content in the overhead distillate of the biobutanol column can effectively reduce the cost of acetone–biobutanol fermentation.

Nowadays, the global optimization is well suited to address a wide range of processes, since it allows to perform energy and economic analysis and to determine the optimal operating conditions in a systematic and rigorous way (Gupta et al. 2015). If one considers a broader view,

however, one may find that such solutions may pose additional environmental burdens somewhere else in the life cycle (Gutierrez-Arriaga et al. 2013). For example, the treatment units required for the process sources may increase the pollution to the environment, or the use of one type of fresh source may reduce the pollution in the plant, but the pollution to treat that fresh source may be higher than the one avoided in the plant. In this context, an overall approach that combines economic and environmental impacts is particularly useful. Life-cycle assessment (LCA) provides a useful tool to evaluate the overall environmental loads associated with a process, product, or activity that identifies and quantifies the raw materials and energy used as well as the wastes released to the environment. The papers by Alexander et al. (2000), Guillén-Gosálbez et al. (2008), and Gebreslassie et al. (2009) presented some applications of the LCA method for some chemical process design problems to improve their environmental performance.

The aim of this work is to perform the process design, multi-objective optimization, and comparison of four different possible process routes for industrial scale to produce biobutanol. Several routes were identified; the routes A, B, and C consisted of a steam stripping distillation and distillation columns, while in the route D, some of the distillation columns were replaced with a liquid–liquid extraction (LLE) column (see Fig. 1). The process was performed in the Aspen Plus software, and the optimization was conducted using the stochastic optimization method of differential evolution (DE) with tabu list (TL), having two objective functions, the total annual cost (TAC) as an economic objective, whereas the environmental objective function is measured through the eco-indicator 99, which is based on the LCA methodology.

Problem statement

There are two basic problems with butanol fermentation: (i) use of dilute sugar solution which results in a dilute product and large disposal loads, and (ii) energy-intensive recovery of butanol from dilute fermentation broth. A solution to these problems can be addressed in two ways: (i) use of genetic engineering techniques to develop strains that could tolerate higher concentration of butanol and sugar to produce higher concentrations of butanol, (ii) use of engineering techniques to ferment and remove the product simultaneously so that a toxic butanol concentration inside the reactor is never reached. The second solution involves the application of engineering techniques to relieve product inhibition and allows using concentrated sugar solutions. The recovery technique should exhibit long-term stability, high selectivity and removal rate, and low cost (García et al. 2011).

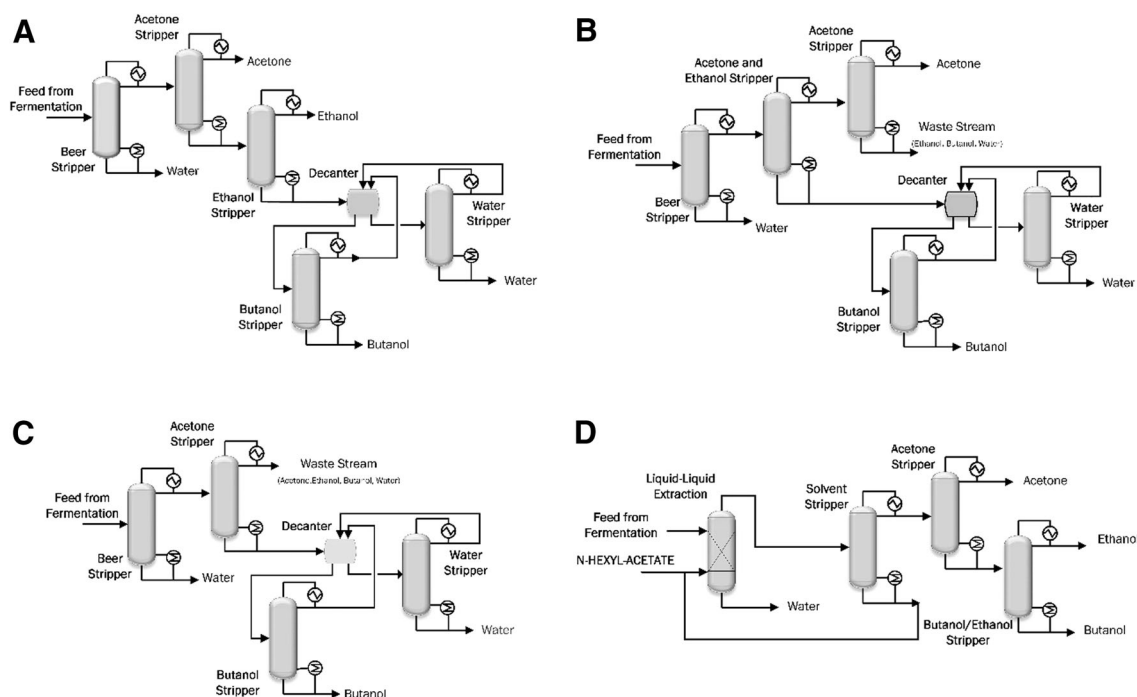


Fig. 1 Processes studied in the recovery of biobutanol

Recently, Van der Merwe et al. (2013) reported four alternatives to purify all the components obtained in the ABE fermentation (Fig. 1). These processing routes employed similar technologies to the ones previously used in industrial processes for the production of biobutanol. Process route A (Fig. 1) was defined using as base case the design simulated by Roffler et al. (1987), where all components from the ABE fermentation are purified. Process route B (Fig. 1) is also based on the process design reported by Roffler et al. (1987). In this process route, the third distillation column does not purify ethanol such as route A does. Process route C (Fig. 1) was defined using the process design reported by Marlatt and Datta (1986). In this design, only the biobutanol flow is purified. Finally, process route D (Fig. 1) is slightly different than process routes A, B, and C, since the first distillation column is replaced with a LLE column, using hexyl acetate as the extractive agent, in order to separate both homogeneous and heterogeneous azeotropes. After these three distillation columns, the separation of acetone, biobutanol, and ethanol is performed.

In a previous work by Sánchez-Ramírez et al. (2015), it was reported that process route D has a minor economic impact, evaluating the TAC in a rigorous optimization process; however, in the present study, these processes have been analyzed under the perspective of a multi-objective optimization approach using two objective functions, the TAC and eco-indicator 99 as the economic and environmental impact indicators, respectively. The application of a multi-objective optimization approach allows

the study of a wider picture of the process performance and a better knowledge of the role of all the variables involved in process design.

In this study, all these design cases were initially simulated using Aspen Plus process models. It should be noted that these process models were robust and thermodynamically rigorous. According to Van der Merwe et al. (2013) and Chapeaux et al. (2008), the NRTL-HOC was the most accurate thermodynamic model for calculating the physical properties for the components used at the specified conditions. It was assumed that all process designs have the same stream feeds except the LLE design where hexyl acetate was added as extractive agent. The product purities were achieved in all process, i.e., at least biobutanol 99.5 % (wt%), acetone 98 % (wt%), and ethanol 95 % (wt%) for process route A; biobutanol 99.5 % (wt%) and acetone 98 % for process route B; biobutanol 99.5 % (wt%) for process route C; biobutanol 99.5 % (wt%), acetone 98 % (wt%), and ethanol 99 % (wt%) for process route D; and at least 95 % (wt%) recovery of ethanol, 99 % (wt%) recovery of acetone and biobutanol, and 99.9 % (wt%) hexyl acetate recovery, respectively.

Optimization problem

The optimized conditions to operate a biobutanol fermentation processes are essential to run a biobutanol industry that can effectively compete with the current biobutanol

Table 1 Decision variables used in the global optimization of process designs for biobutanol production

Concept	Process design A	Process design B	Process design C	Process design D
Number of stages C1	X	X	X	X
Number of stages C2	X	X	X	X
Number of stages C3	X	X	X	X
Number of stages C4	X	X	X	X
Number of stages C5	X	X		
Feed stages C1	X	X	X	X
Feed stages C2	X	X	X	X
Feed stages C3	X	X	X	X
Feed stages C4	X	X	X	X
Feed stages C5	X	X		
Reflux ratio C1	X	X	X	
Reflux ratio C2	X	X	X	X
Reflux ratio C3	X	X	X	X
Reflux ratio C4	X	X	X	X
Reflux ratio C5	X	X		
Distillate rate C1	X	X	X	
Distillate rate C2	X	X	X	X
Distillate rate C3	X	X	X	X
Distillate rate C4	X	X	X	X
Distillate rate C5	X	X		
Diameter C1	X	X	X	X
Diameter C2	X	X	X	X
Diameter C3	X	X	X	X
Diameter C4	X	X	X	X
Diameter C5	X	X		
Total	25	25	20	17

Table 2 Unit eco-indicator used

Impact categories	Steel (points/kg)	Steam (points/kg)	Electricity (points/kWh)
Carcinogenics	6320E−03	1180E−04	4360E−04
Climate change	1310E−02	1600E−03	3610E−06
Ionizing radiation	4510E−04	1130E−03	8240E−04
Ozone depletion	4550E−06	2100E−06	1210E−04
Respiratory effects	8010E−02	7870E−07	1350E−06
Acidification	2710E−03	1210E−02	2810E−04
Eco toxicity	7450E−02	2800E−03	1670E−04
Land occupation	3730E−03	8580E−05	4680E−04
Fossil fuels	5930E−02	1250E−02	1200E−03
Mineral extraction	7420E−02	8820E−06	57EE−6

derived from the petrochemical route. Also, the environmental impact must be taken in count in order to satisfy the governmental restrictions. The environmental impact is quantified using LCA principles, an approach that leads to solutions in which the overall environmental damage is globally minimized.

Economic objective function

Process route A and B

In process designs A and B, the objective function is the minimization of the TAC, which is proportional to the heat

Table 3 Results of the global optimization of TAC for the process designs A

Process design A	Point 3					Point 2					Point 1				
	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5
Column topology															
Number of stages	51	46	43	36	7	17	38	43	37	23	12	34	51	38	19
Feed stage	48	28	24	26	6	11	22	18	7	5	4	22	24	24	16
Specifications															
Distillate rates (lbmol/h)	1.58	1.73	1.71	0.57	0.63	1.58	1.73	1.71	0.59	0.77	1.58	1.73	1.71	0.71	0.70
Reflux ratio	1.23	16.06	122.91	11.62	2.09	1.09	20.60	85.00	11.09	2.27	1.81	22.35	93.73	20.03	2.66
Diameter (ft)	4.69	1.93	3.21	3.60	2.73	1.61	4.19	2.32	2.43	1.56	1.07	1.79	1.22	1.65	1.64
Feed streams															
Acetone flow rate (lb/h)	16.95					16.95					16.950				
Butanol flow rate (lb/h)	30.18					30.18					30.181				
Ethanol flow rate (lb/h)	0.729					0.729					0.729				
Product streams															
Acetone purity (wt%)		0.999					0.999					0.999			
Butanol purity (wt%)				0.9997						0.9946				0.9942	
Ethanol purity (wt%)			0.9389					0.9399					0.9389		
Energy requirements															
Reboiler duty (BTU/h)	92,174	65788	38,129	131,604	52,382	87,099	83,157	26,192	131,413	59,066	113,021	89,904	28,721	271,303	64,379
Condenser duty (BTU/h)	-80,260	-64,981	-38,103	-128,440	-49,027	-75,185	-82,351	-26,165	-128,214	-55,314	-101,108	-89,098	-28,694	-267,938	-60,833
Economic evaluation															
Capital cost (\$)	396,659	100,783	240,962	172,147	122,428	40,303	170,288	109,133	68,836	43,362	31,447	54,826	51,740	52,044	42,143
Total annual cost (\$/year)			764,771					482,236					305,781		
Environmental impact															
Eco-indicator 99 (points/year)			22,345					22,747					33,353		

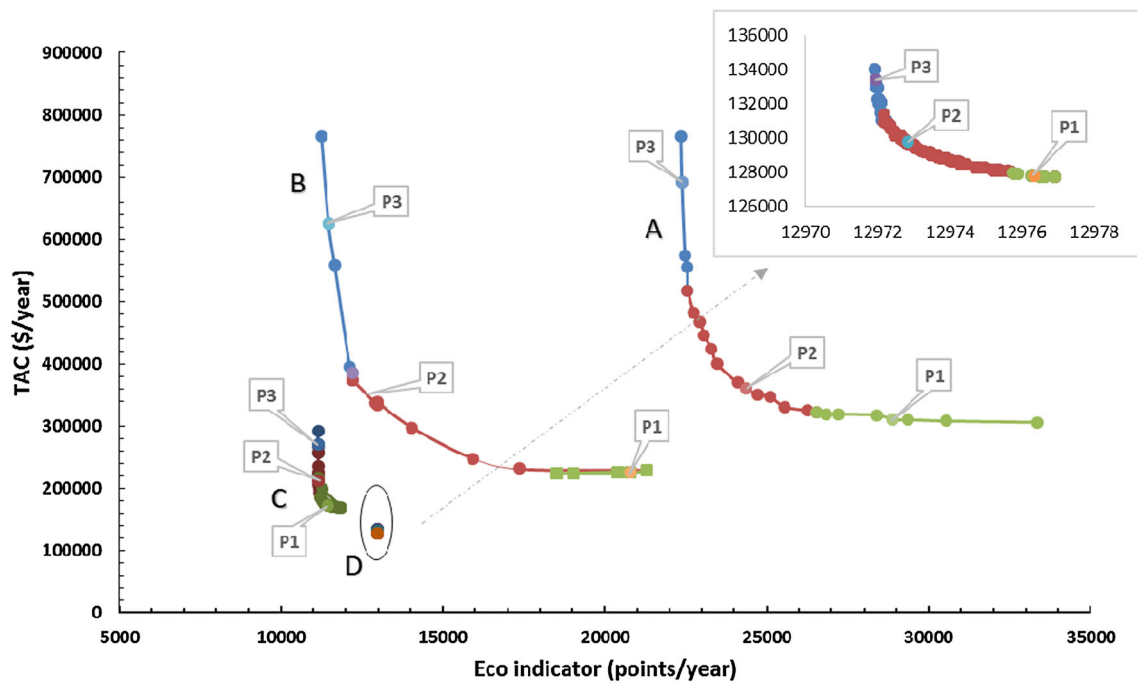


Fig. 2 Pareto fronts of each process route analyzed

duty, services, and column size. The minimization of this objective is subjected to the required recoveries and purities in each product stream, which is stated as follows:

$$\begin{aligned} \text{Min (TAC)} &= f(N_{\text{tn}}, N_{\text{fn}}, R_{\text{m}}, F_{\text{m}}, D_{\text{cn}}) \\ \text{Subject to } \vec{y}_{\text{m}} &\geq \vec{x}_{\text{m}} \end{aligned} \quad (1)$$

where N_{tn} are the total column stages, N_{fn} is the feed stages in column, R_{m} is the reflux ratio, F_{m} is the distillate fluxes, D_{cn} is the column diameter, $\vec{y}_{\text{m}}$ and $\vec{x}_{\text{m}}$ are vectors of obtained and required purities for the m components, respectively. This minimization implies the manipulation of 25 continuous and discrete variables as freedom degrees for each route, where five variables are used for the design of each column. It should be noted that since the product stream flows are manipulated, the recoveries of the key components in each product stream must be included as a restriction for the optimization problem. In the process route A, the acetone, biobutanol, and ethanol must be recovered, while in the process route B, the acetone and biobutanol must be recovered.

Process route C

This process route has also one objective function. The minimization of this objective is subject to the required recoveries and purities in each product stream, and the optimization problem is defined as follows:

$$\begin{aligned} \text{Min (TAC)} &= f(N_{\text{tn}}, N_{\text{fn}}, R_{\text{m}}, F_{\text{m}}, D_{\text{cn}}) \\ \text{Subject to } \vec{y}_{\text{m}} &\geq \vec{x}_{\text{m}} \end{aligned} \quad (2)$$

This optimization problem implies the manipulation of 20 decision variables for each process route. It should be noted that the difference between this route and routes A and B is the purities in acetone and ethanol product streams, and the recovery of the same components.

Process route D

This route has also the same objective function. Nevertheless, since the first distillation column is replaced with a LLE extraction column, the number of decision variables is reduced in that column. The optimization problem is defined as follows:

$$\begin{aligned} \text{Min (TAC)} &= f(N_{\text{tn}}, N_{\text{fn}}, R_{\text{m}}, F_{\text{m}}, D_{\text{cn}}) \\ \text{Subject to } \vec{y}_{\text{m}} &\geq \vec{x}_{\text{m}} \end{aligned} \quad (3)$$

Overall, 17 decision variables are considered in the design of this process route, where two design variables are related to the LLE column. All design variables for the case studies are described in Table 1.

Environmental objective function

The EI is measured through the eco-indicator 99, which is based on the methodology of the life-cycle analysis and is stated as follows:

$$\text{Min (Eco-indicator)} = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (4)$$

Table 4 Results of the global optimization of TAC for the process design B

Process design B	Point 3					Point 2					Point 1				
	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5	C1	C2	C3	C4	C5
Column topology															
Number of stages	9	62	68	5	17	17	38	43	37	23	12	34	51	38	19
Feed stage	8	31	51	2	16	11	22	18	7	5	4	22	24	24	16
Specifications															
Distillate rates (lbmol/h)	2.050	0.311	0.291	0.553	0.520	2.052	0.311	0.291	0.566	0.520	2.053	0.314	0.291	0.576	0.520
Reflux ratio	0.604	9.396	8.583	0.770	1.054	0.138	8.728	10.255	1.620	1.062	0.086	7.862	16.947	2.208	1.013
Diameter (ft)	3.351	3.313	4.579	3.239	1.455	1.857	2.094	1.056	4.585	2.451	1.369	1.172	1.168	2.616	1.083
Feed streams															
Acetone flow rate lb/h	16.95					16.950					16.95				
Butanol flow rate (lb/h)	30.18					30.18					30.18				
Ethanol flow rate (lb/h)	0.729					0.729					0.729				
Product streams															
Acetone purity (wt%)			0.996					0.9986					0.9986		
Butanol purity (wt%)				0.999					0.999					0.999	
Ethanol purity (wt%)			0.8681					0.8613					0.8003		
Energy requirements															
Reboiler duty (cal/h)	65,686	42,280	35,423	23,019	24,274	48,475	40,212	41,569	32,253	24,371	46,667	37,132	66,279	38,867	23,896
Condenser duty (cal/h)	-59,113	-41,672	-35,446	-17,695	-19,293	-41,966	-39,002	-41,593	-26,851	-19,367	-40,097	-35,920	-66,306	-33,449	-18,908
Economic evaluation															
Capital cost (\$)	58,241	251,569	349,976	41,570	38,076	35,297	90,255	48,463	58,438	48,588	30,581	43,703	43,648	37,038	30,618
Total annual cost (\$/year)			764,519					305,560					213,456		
Environmental impact															
Eco-indicator 99 (point/year)			10,245					10,986					20,388		

Table 5 Results of the global optimization of TAC for the process design C

Process design C	Point 3				Point 2				Point 1			
	C1	C2	C3	C4	C1	C2	C3	C4	C1	C2	C3	C4
Column topology												
Number of stages	23	66	5	62	7	37	22	24	7	37	22	24
Feed stage	14	20	4	13	6	35	14	17	6	35	14	17
Specifications												
Distillate rates (lbmol/h)	1.589	1.619	0.418	0.591	1.587	1.619	0.423	0.584	1.585	1.619	0.420	0.588
Reflux ratio	1.023	4.352	74.350	1.350	1.031	4.354	28.986	1.365	1.070	5.659	44.450	1.655
Diameter (ft)	2.171	1.802	1.745	1.412	1.419	1.232	1.428	1.021	1.052	1.160	1.447	1.246
Feed streams												
Acetone flow rate lb/h	16.950				16.950				16.950			
Butanol flow rate (lb/h)	30.181				30.181				30.181			
Ethanol flow rate (lb/h)	0.729				0.729				0.729			
Product streams												
Acetone purity (wt%)		0.850				0.848				0.846		
Butanol purity (wt%)				0.999				0.999			0.036	0.999
Ethanol purity (wt%)			0.037				0.036					
Energy requirements												
Reboiler duty (cal/h)	84,477	32,819	20,477	32,412	84,820	33,035	20,813	32,016	86,294	41,180	22,904	32,234
Condenser duty (cal/h)	-72,555	-32,308	-17,673	-29,189	-72,901	-32,528	-18,001	-28,818	-74,376	-40,676	-20,102	-29,026
Economic evaluation												
Capital cost (\$)	56,812	84,625	72,086	55,995	45,425	52,327	49,908	36,052	33,182	47,040	34,896	29,850
Total annual cost (\$/year)	291,883				206,143				168,935			
Environmental impact												
Eco-indicator 99 (points/year)	11,141				11,170				11,871			

Table 6 Results of the global optimization of TAC for the process design D

Process design D	Point 3				Point 2				Point 1			
	LLE	C2	C3	C4	LLE	C2	C3	C4	LLE	C2	C3	C4
Column topology												
Number of stages	4	24	50	56	4	23	45	43	4	23	45	31
Feed stage		12	31	13		13	31	13		12	30	12
Specifications												
Distillate rates (lbmol/h)		0.716	0.294	0.015		0.716	0.294	0.015		0.716	0.294	0.015
Reflux ratio		0.900	6.000	9.581		0.900	6.000	9.638		0.900	6.000	9.954
Diameter (ft)	1.008	0.967	0.945	0.997	1.008	0.953	0.942	0.944	0.990	0.940	0.941	0.941
Feed streams												
Acetone flow rate lb/h	16.950				16.950				16.950			
Butanol flow rate (lb/h)	30.181				30.181				30.181			
Ethanol flow rate (lb/h)	0.729				0.729				0.729			
Hexyl acetate flow rate (lb/h)	1568.379				1568.382				1568.397			
Product streams												
Acetone purity (wt%)		0.998				0.998				0.998		
Butanol purity (wt%)				0.999				0.999				0.999
Ethanol purity (wt%)			0.995				0.995				0.996	
Energy requirements												
Reboiler duty (cal/s)		225,634	225,634	225,637		27,473	27,474	27,475		2786	2799	2880
Condenser duty (cal/s)		-24,782	-24,782	-24,782		-26,322	-26,323	-26,324		-2690	-2703	-2783
Economic evaluation												
Capital cost (\$)	2275	29,296	33,481	35,045	2303	29,046	32,558	32,210	2254	28,997	32,550	30,000
Total annual cost (\$/year)		134,033				130,055				127,749		
Environmental impact												
Eco-indicator 99 (points/year)		12,971			12,972					12,976		

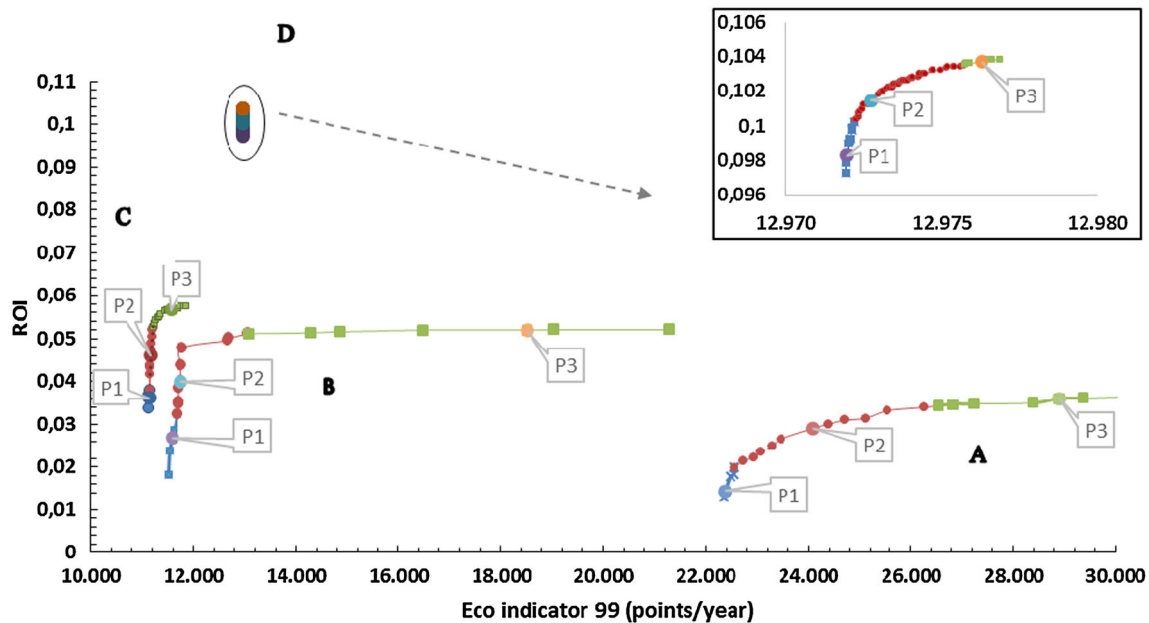
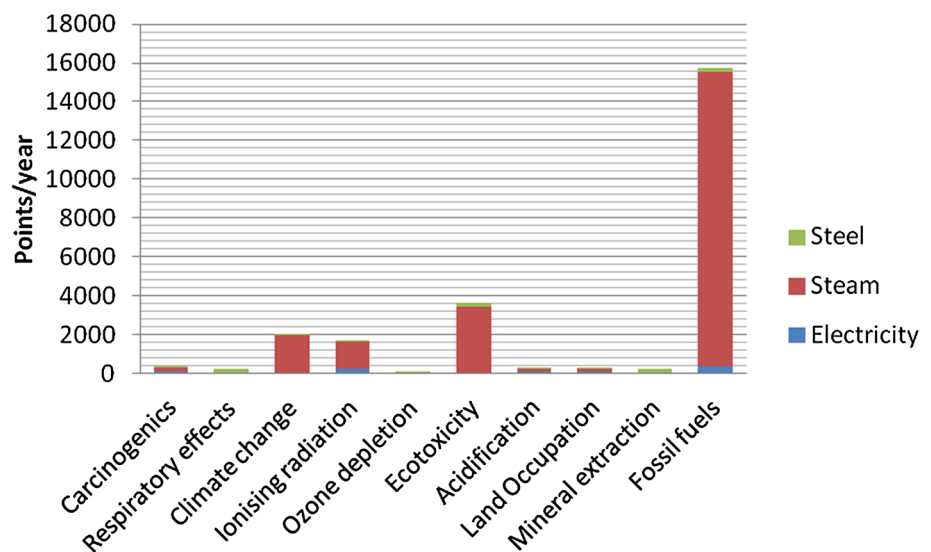


Fig. 3 Pareto fronts evaluating the ROI

Fig. 4 Annualized environmental impact of point three in process route A



where b_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in category d , and δ_d is the normalization factor for damage of category d .

Additionally, it was implemented a comparative scenario where all the steam needed as heat duty in each distillation column was replaced by solar collectors, and this scenario was performed based on that almost all the greenhouse gas emissions are associated with the use of fossil fuels. Furthermore, considering that each solar collector has its own economic impact, a new Pareto is

developed, where the TAC includes the costs for purifying and the solar collector cost. It should be noted that this scenario with a solar collector has almost zero greenhouse gas emission. A comprehensive description of this method is provided by Lira-Barragan et al. (2013).

Global stochastic optimization strategy

Particularly, the optimization and design of processes routes are highly non-linear and multivariable problems, with the presence of both continuous and discontinuous design variables. Also, the objective functions used as the optimization

Fig. 5 Annualized environmental impact of point one in process route A

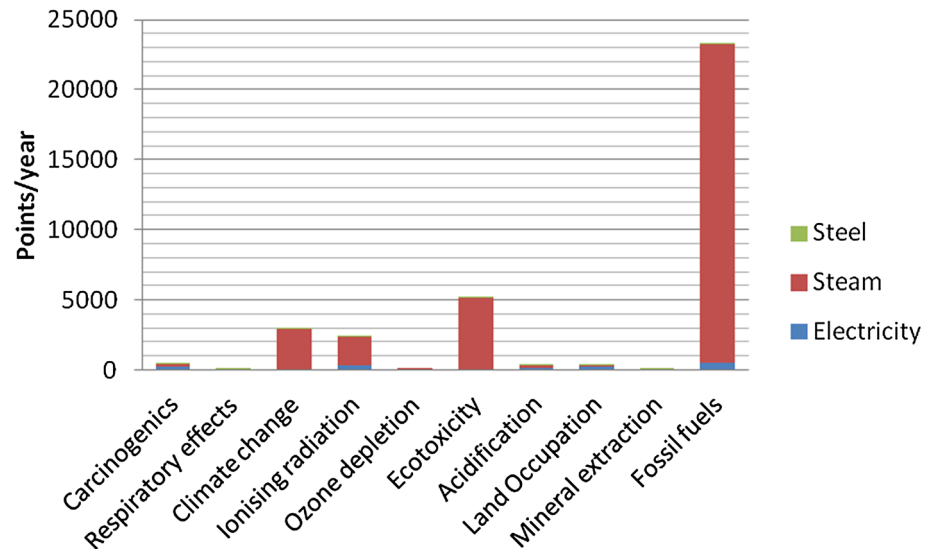
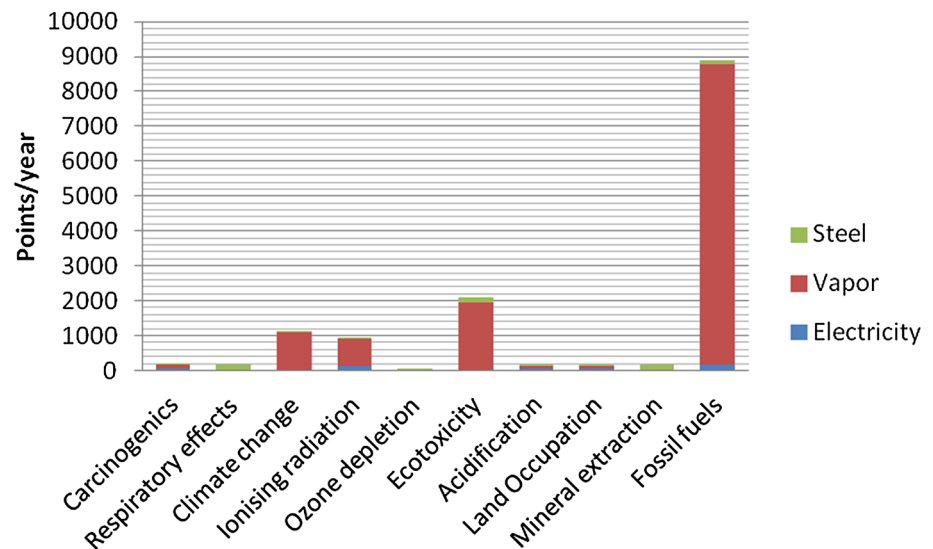


Fig. 6 Annualized environmental impact of point three in process route B



criteria are potentially non-convex with the possible presence of local optimums and subject to several constraints.

Then, in order to optimize the processes routes for biobutanol production, a stochastic optimization method was used, in this case, the DE with tabu list (DETL) method (Srinivas and Rangaiah 2007). This method showed that the use of some concepts of the metaheuristic tabu can improve the performance of the DE algorithm. In particular, the TL can be used to avoid the revisit of search space by keeping record of the recently visited points, which can avoid unnecessary function evaluations. Based on this fact, the hybrid method DETL is proposed. A comprehensive description of this DETL algorithm is provided by Srinivas and Rangaiah (2007).

The implementation of this optimization approach was made using a hybrid platform using Microsoft Excel and

Aspen Plus. The vector of decision variables (i.e., the design variables) is sent to Microsoft Excel to Aspen Plus using dynamic data exchange (DDE) through a COM technology. In Microsoft Excel, these values are attributed to the process variables that Aspen Plus needs. After the simulation, Aspen Plus returns to Microsoft Excel the resulting vector. Finally, Microsoft Excel analyzes the values of the objective function and proposes new values of decision variables according to the used stochastic optimization method. For the optimization of the process routes analyzed in this study, the following parameters are used for the DETL method: 200 individuals, 500 generations, a TL of 50 % of total individuals, a tabu radius of 0.0000025, and 0.80 and 0.6 for crossover and mutation fractions, respectively. These parameters were obtained through a tuning process via preliminary calculations. The tuning

Fig. 7 Annualized environmental impact of point one in process route B

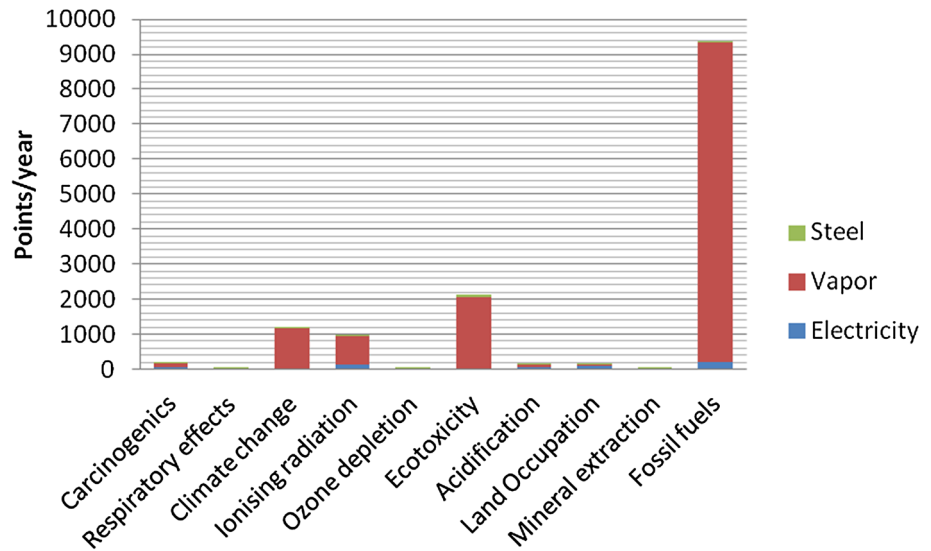
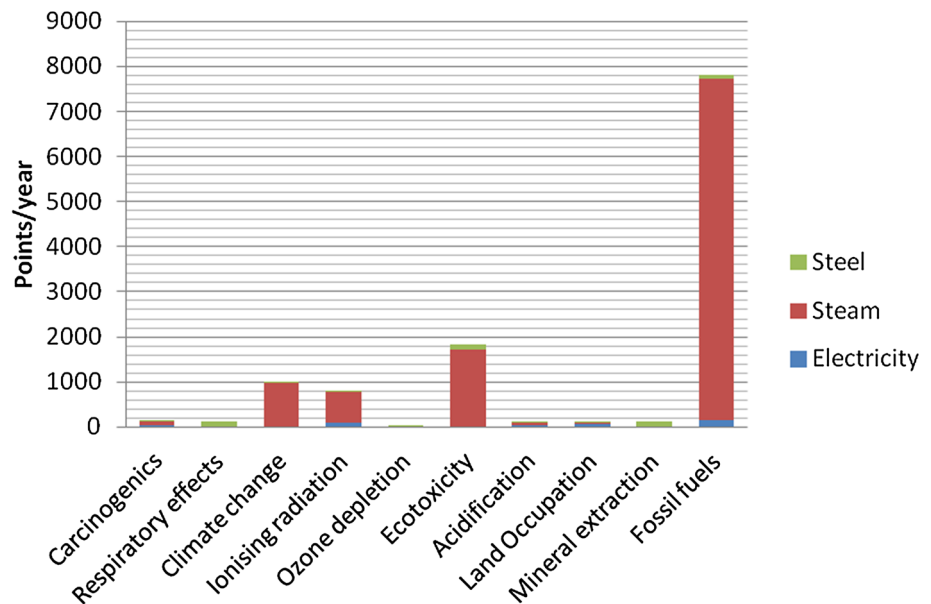


Fig. 8 Annualized environmental impact of point three in process route C



process consists of performing several runs with different number of individuals and generations, in order to detect the best parameters that allow obtaining the better convergence performance of the DETL method.

In order to calculate the TAC used as the objective function, the method published by Guthrie (1969) and improved by Ulrich (1984) was used. It performs cost estimations of an industrial plant separated in units, and using equations published by Turton et al. (2009), the cost approximation of the process is given in Eq. (5):

$$TAC = \frac{\sum_{i=1}^n C_{TM,i}}{n} + \sum_{j=1}^n C_{ut,j}, \quad (5)$$

where TAC is the total annual cost, C_{TM} is the capital cost of the plant, n is the total number of individual units, and C_{ut} is the utility cost.

Furthermore, considering that in engineering applications, the evaluation of projects is also performed using some other measures different than the TAC, the return of investment (ROI) is also calculated (Bagajewicz 2008). This measure is aimed at reducing the complex process of cash flow that takes place in different periods of time in the future to one single number. The ROI is defined in its most simplified form as follows:

$$ROI = \frac{(\sum_{i=1}^N CF_i)/N}{I}, \quad (6)$$

Fig. 9 Annualized environmental impact of point one in process route C

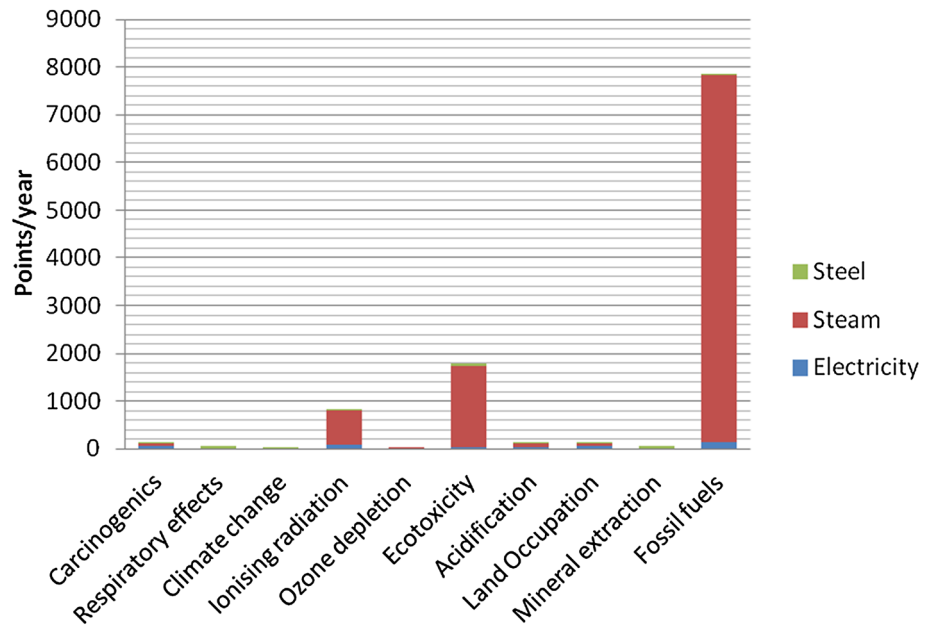
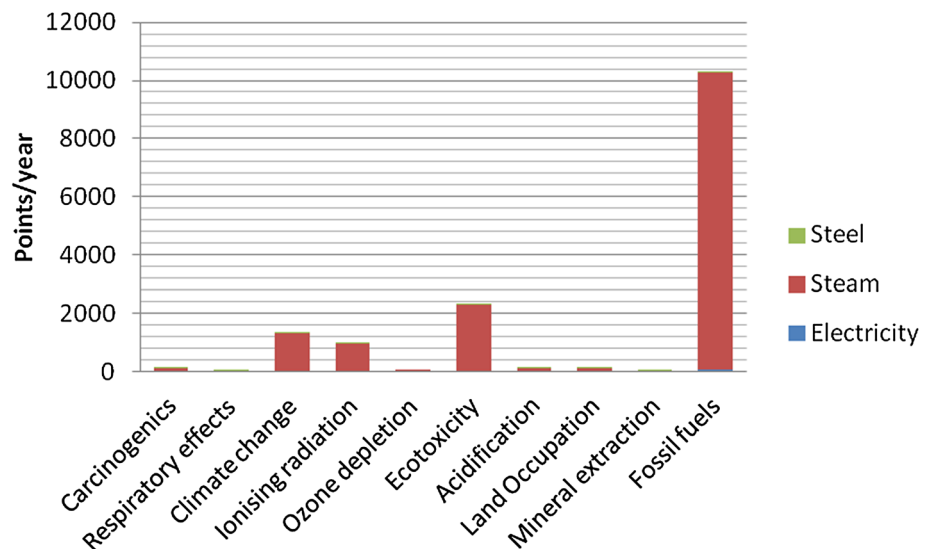


Fig. 10 Annualized environmental impact of point three in process route D



where N is the number of years of the project and an average value of the after tax revenues is used. By dividing by the investment, one can obtain the rate at which the investment is recovered.

In the eco-indicator 99 methodology, 11 impact categories are considered (Geodkoop and Spriensma 2001). These 11 categories are included into three major damages categories: (1) human health, (2) ecosystem quality, and (3) resources depletion (see Table 2). We considered as sources of impact: the steam used in reboiler as duty, the steel to construct the equipment, and the electricity used to pump the cooling water.

Results

Before the optimization process, all sequences were modeled and simulated rigorously in Aspen Plus using the RadFrac module. This means that all the presented designs were obtained considering the complete set of MESH (mass balances, equilibrium relationships, summation constraints, energy balance) equations along with the phase equilibrium calculations. Figure 2 shows the convergence behavior of the objective functions used for the process optimization. Results are presented until 100,000 evaluations because the vector of decision variables does not

Fig. 11 Annualized environmental impact of point one in process route D

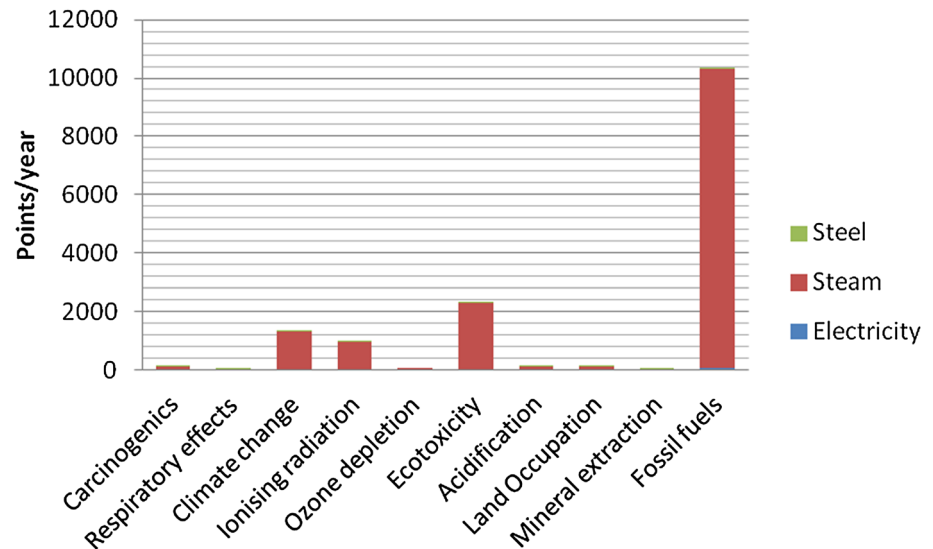


Table 7 Useful collected energy per month for ETSC collector

Month/type of solar collector	ETSC (kJ/m ² month)
January	245,576
February	265,81
March	346,518
April	343,116
May	333,461
June	272,646
July	266,166
August	263,655
September	236,682
October	246,58
November	244,458
December	235,03

produce a significant improvement. Under this scenario, it was assumed that DETL achieved the convergence at the tested numerical conditions and the reported results correspond to the best solution obtained by the DETL method.

The Pareto fronts obtained after the optimization process are shown in Fig. 2, also in Fig. 2 can be identified three zones in each Pareto front, one part where it is localized the most expensive designs but with the minor environmental impact, contrary it can be seen zones where all the designs have the smallest TAC, nevertheless the eco-indicator is the biggest. At the middle of both zones is located a feasible zone for all processes, all those designs accomplish the purities, and recoveries required and their TACs and eco-indicators 99 are compensated. The shape of each Pareto front in Fig. 2 represents the conflicting targets along optimization process, in a rough explanation, the blue zone

in Pareto front in built by designs which preferably include the biggest number of stages (see Tables 3, 4, 5, 6), the biggest diameter of column but the minor heat duty, these combinations produced the biggest TAC but the smallest eco-indicator 99. The green zone consists of designs which preferably include the minor number of stages, the smallest diameter of column, however the biggest heat duty, which produced the lowest TAC but the biggest eco-indicator 99. At middle of both zones, the red zones include design with average variables between both zones, which is reflected in the TAC and eco-indicator values.

Comparing the results among all the four processes routes, it is clear that process route D has the smallest TAC due to the incorporation of a LLE column where water is split with null heat duty. On the other hand, process route A, where all components are purified, has the biggest TAC, followed by process routes B and C, respectively; in this way, the reduction in TAC among these processes routes is due to the purification of acetone and ethanol; however, the purification of ethanol represents a huge economic impact that can be seen comparing process routes B and C. On the other hand, despite process route D exhibited the minor TAC, the resulted eco-indicator is not the smallest, this place own to process route C, where only biobutanol is purified. The difference in the environmental impact between Pareto fronts C and D is quite small. This difference could be due to the size of the distillation column (number of stages). In other words, the optimization of process route D converged preferably in bigger columns comparing with process route C, and the contribution for the used steel in each column of process C makes the difference among them.

A comparison between the results from a previous work presented by Sánchez-Ramírez et al. (2015) was made. In

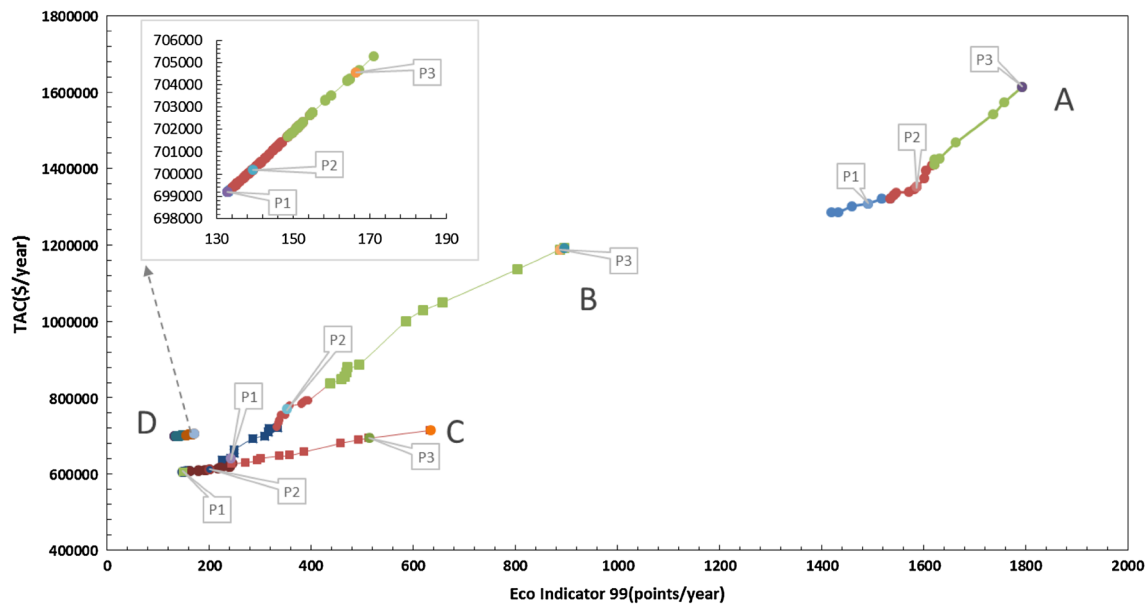


Fig. 12 Pareto fronts of each process route considering solar collectors

this work, they concluded that process route D has the smallest economic impact measured through TAC as objective function. This study confirms that process route D has much more economic and environmental potential compared with process routes A, B, and C. However, it must be known that the algorithm has explored a different multivariable function since the inclusion of the eco-indicator 99 model, which is loaded with its function, constraints, and so on. In this way, through the optimization process, the best solutions can be obtained considering both economic and environmental targets (both conflicting targets), not as the previous results where any other targets were neglected and only the economic target was considered. In process route D, the TAC values were not considered as an improvement since the optimal design obtained by Sánchez-Ramírez et al. (2015) could be placed at the top of the Pareto front presented in this work.

Another economic point of view is the evaluation of the ROI in each process route. Figure 3 presents the ROI of all four processes and it is totally consistent with Fig. 2; in this case, process route D, as in the last figure, has the best economic results, and the other three process routes show a bad economic conditions under this scenario and in current conditions. Nevertheless, process route D did not show the best results when the eco-indicator 99 is evaluated; in the same way as Fig. 4, process route C overcomes to process route D. In this way, it would be quite interesting to propose a new intensified design based on the process route D. This new design could be synthesized by considering some well-studied process intensification methodologies (Ponce-Ortega et al. 2012; Chouinard-Dussault et al. 2011).

Obviously, there are expected energy savings, leading to new improved designs. Furthermore, it is clear that in this analysis, only two objective functions are considered: the economic and environmental impacts. However, an important point of view must be analyzed in future work such as dynamic behavior, i.e., the dynamic properties of this kind of process under composition or feed disturbances.

Moreover, Figs. 4, 5, 6, 7, 8, 9, 10, and 11 present the environmental impact of all Pareto fronts ends, and there can be seen the great impact related with the use of steam in all these processes; another ten categories contribute each one with few less order of magnitude comparing with steam. Electricity and steel impacts are slightly bigger at the point where the minor environmental impact is, comparing with the other extremes of the Pareto front. Obviously, the end of the Pareto, which has the minor TAC, has a bigger environmental impact, and also the most expensive point has the contrary behavior in this categories. In other words, the environmental impact of this type of processes is influenced by the use of steam. One contribution of this work is the comparison and proposal of a scenario where this steam could be supplied from another source of energy. An option for this scenario could be the inclusion of a solar collector.

This hypothetical alternative shows a broader vision where all greenhouse gas emissions could be drastically diminished, and this is considering a zero emissions from the solar collector (Sánchez-Bautista et al. 2015); nevertheless, the economic impact will have a very important effect in a new Pareto front since steam contributions are null.

Then, from the methodology provided by Lira-Barragan et al. (2013), and considering an hypothetically location of this project in Morelia, Mexico, latitude of $19^{\circ}42'$ and a longitude of $101^{\circ}11'$ (see Table 7), the area of an evacuated tube solar collector (ETSC) for each process route was calculated, and also the TAC is recalculated adding its own collector, and similarly the eco-indicator 99 is recalculated considering zero gas emissions replacing the use of fossil fuel. Thereby, in Fig. 12 is shown a new Pareto front where it is included the new values of TAC and eco indicator 99, it is clear that the main impact in the eco-indicator 99 was the use of steam from fossil fuels, then in this case where a solar collector is included, this huge impact would be removed, nevertheless there is a great increase in the TAC, comparing with the first scenario (Fig. 2). Additionally, the process route A showed again the worst behavior due to having the biggest TAC and heat duty.

This new scenario shows that probably the use of this solar technologies is not as good as we thought with the current economic situation. Although the environmental impact is diminished substantially, the economic scenario is wide affected. This increment of the TAC of each process route would impact directly on the final price and consume of butanol. Nevertheless, a sum of efforts in several sources of knowledge will lead us to a better technologies and improved process that could compete with butanol produced by petrochemical routes.

Conclusions

In this study, a stochastic global optimization method for the process design of several routes for the production of biobutanol has been presented. According to the obtained results, process route D has showed the smallest TAC. Process route A, where all components are purified, showed the biggest TAC due to the capital cost of equipment and heat duty performing ABE purification. Considering the environmental impact measured by the eco-indicator 99, process route C showed the minor impact, followed very close by process route D, with a slightly difference in column size, diameter, and heat duty.

Evaluating the ROI, process route D showed the best scenarios near a ROI of 0.1, moved away completely from the other three process routes. Under this scenario, process design C showed the minor impact measured through the eco-indicator 99, followed closely again by process route D.

Considering the inclusion of a solar collector, avoiding the use of steam from fossil fuels, values for the eco-indicator 99 showed a huge decrease; however, at the same time, there is an increase of the TAC, showing in this way a new and totally different scenario where the environmental impact is small at expenses of a bigger economic impact in each process.

Moreover, it would be interesting to determine the dynamic behavior of these designs in order to identify all their process advantages and disadvantages. Furthermore, this type of research efforts combined with results of other studies could lead in future years to a profitable ABE fermentation process, which could compete with traditional ways to produce biobutanol.

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