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DOI
10.1016/B978-0-12-823377-1.50099-9

Publication date
2020

Document Version
Final published version

Published in
Computer Aided Chemical Engineering

Sauro Pierucci, Flavio Manenti, Giulia Bozzano, Davide Manca (Eds.)
Proceedings of the 30[th] European Symposium on Computer Aided Process Engineering
(ESCAPE30), May 24-27, 2020, Milano, Italy.
http://dx.doi.org/10.1016/B978-0-12-823377-1.50099-9

Assessing the Sensitivity of Technical Performance of three Ethanol Production Processes based on the Fermentation of Steel Manufacturing Offgas, Syngas and a 3:1 Mixture Between H_2 and CO_2

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Abstract

This study assesses the sensitivity of the technical, environmental and economic performance of three ethanol production process based on the fermentation of three gas mixtures: i) CO-rich flue gas from steel manufacturing, ii) biomass-based syngas with a H_2/CO ratio of 2 and iii) a 3:1 combination between H_2 and CO_2. The sensitivity analysis is based on stochastic bioreactor simulations constructed by randomly generated combinations of eight parameters that command the fermentation process i.e., temperature, pressure, gas feed dilution with an inert components, ethanol concentration, height of the liquid column, mass transfer coefficients, superficial gas velocity and, acetic acid co-production.

The sensitivity analysis identified that the bioreactor technical performance is highly sensitive to variations on pressure, liquid column height and the mass transfer coefficients. The pressure mainly improves mass transfer and consequently ethanol productivity whereas liquid column height improves the gas residence time and consequently the efficiency in the gas utilization. The trend was common for the three gas supply options. The results suggested that in order to produce an optimal bioreactor design, there are options to optimize the productivity and the gas utilization simultaneously.

The results from the sensitivity analysis may help guiding a subsequent multi-objective process optimization study.

Keywords: ethanol, syngas fermentation, sensitivity analysis, stochastic simulation.

1. Introduction

Prevention of global warming is currently pushing global policy-making towards the reduction of CO_2 emissions, which are mostly derived from the combustion of fossil fuels (Boden et al., 2013). Lignocellulosic biomass is seen as an alternative sources of fuels and chemicals that during their life cycle may result in lower carbon emissions (Liu et al., 2017). These feedstocks are abundant and renewable and can be thermochemically converted into gas mixtures containing mainly CO, H_2, CO_2 (Heidenreich and Foscolo,

2015; Matsakas et al., 2017). The gas is commonly referred as syngas and can be used as feedstock for fermentations (Kundiyana et al., 2010).
Only limited details about the industrial process performance have been made public. What has been reported is that microbial selectivity for ethanol falls around 95 % and that gas utilization overpasses 90 % (Simpson, 2018); additionally, it is argued that the exist an energy surplus generated from the based fermentation of syngas (Handler et al., 2016). Moreover, the claims that ethanol concentration in the fermentation media could be held above 50 g/L and overhead pressure should not overpass 3 atm (Li et al., 2017; Trevethick et al., n.d.) have been patented.
In consequence, a mathematical model was developed and reported elsewhere [Almeida, forthcoming] to simulate ethanol production in a bubble column bioreactor fed by CO, H_2 and CO_2 mixtures. That model is used to quantify the sensitivity of the bioreactor technical performance to certain parameters that command the fermentation step. The assessment is applied to three different gas feed compositions.

2. Methodology

2.1. Process configurations

The three process configurations which have been considered in this study differ on the gas production processes: CO-rich BOF offgas from the steel-manufacturing process; *ii)* a 3:1 mixture between H_2 and CO_2, and *iii)* syngas with a H_2/CO ratio of 2.
The fermentation process consists on a bubble column bioreactor fed by the gas mixture. The ethanol produced inside the fermentor is at all times given two possible exit routes *i.e. i)* pre-concentrated along the offgas, where it is subsequently condensed and recovered from by flash separation, and *ii)* along a liquid broth outflow. Acetic acid, also exits the bioreactor along the liquid outflow. The alcohol is distilled out of the two streams by atmospheric distillation and finally dehydrated. The unconsumed gas is here treated as waste and combusted before being released into the atmosphere, as proposed by Handler et al, 2016 (Handler et al., 2016).

2.2. Simulation of the fermentation processes

The simulation of the bioreactor uses a model previously presented elsewhere [Almeida, forthcoming]; therefore, only the basic structure of such model is introduced here.

2.2.1. Simulation of the fermentations of BOF offgas and the H_2/CO_2 mixture

The fermentation model for these two cases is formed by *i)* a black-box model of the main reactions carried out by acetogenic bacteria and *ii)* a mass transfer model of the large bubble column bioreactor. The stoichiometry of the microbial metabolic reaction is constructed by the combination of the catabolic and anabolic reactions.
Ethanol and acetic acid are the products of catabolism, thermodynamically powered by the uptake of the electron donors, CO and H_2. Cells are produced during anabolism. The Gibbs free energy harvested from the electron donors (CO and H_2) during catabolism powers cells. The uptake of CO and H_2 are assumed to follow hyperbolic kinetics. The maximum uptake rate of the electron donors is estimated using thermodynamics (Heijnen, 2013).
Mass transfer in the bioreactor is simulated assuming the process operates in continuous mode at steady-state (Heijnen and van't Riet, 1984; van't Riet and Tramper, 1991). Mass transfer is driven by the energy input provided by the gas sparging [42]. A system of non-linear equations formed by the mass balances is solved by a constrained optimization of the volumetric ethanol productivity (R_{et}).

2.2.2. Simulation of the fermentation of biomass-derived syngas

Since the black-box model of microbial reactions is only able to simulate the consumption of either CO or H_2, the simulation of biomass-derived syngas (BDS) consumption is done indirectly adding the mass and energy streams contributions from CO fermentation (the BOF offgas case) and H_2/CO_2 fermentation cases. The H_2/CO ratio in syngas is assumed to be 2.

2.3. Process assessment and performance indicators

The ethanol production processes are evaluated from the perspective of the bioreactor technical performance through the ethanol volumetric productivity (R_{et}) and gas utilization (U_S), defined as the percent change on the gas molar flow rate of electron donors across the fermentor.

2.4. Stochastic simulation of the bioreactor

The operation of the bioreactor is simulated under 5000 randomly generated combinations of eight input parameters, which are considered to command the bioreactor performance *i.e., i)* process temperature (T), *ii)* top reactor pressure (p_t), *iii)* gas feed dilution (f_{Dil}), *iv)* maximum ethanol concentration (C_{et}^{max}), *v)* liquid column height (h_L), *vi)* mass transfer coefficient factor (f_{k_La}), *vii)* acetic acid production factor (f_{Ac^-}) and *viii)* the pressure-corrected superficial gas velocity (v_{sG}^c). See Table 1.

Table 1 Maximum and minimum values used the input parameters in the stochastic bioreactor simulation

Input parameter	T [°C]	p_t [atm]	f_{Dil} [%vol.]	C_{et}^{max} [g/L]	h_L [m]	f_{k_La} [-]	f_{Ac^-} [%]	v_{sG}^c [m/s]
Minimum value	27	0.5	0	30	8	0.5	0	0.07
Maximum value	67	3.5	45	120	64	2.0	0.15	0.14

2.5. Sensitivity analysis

The sensitivity of bioreactor and overall process performance indicators (or output parameters - OP) is evaluated using standardized regression coefficients since it offers "a good approximation to a global sensitivity with affordable computational demand" (Morales-Rodriguez et al., 2012), and allows establishing a hierarchical classification of the model IP's according to the level of impact on a determined OP. This method implies that process performance has a linear relation with each input parameter (IP). The reliability of the regression coefficients is evaluated using coefficients of determination (R^2).

3. Results and discussion

3.1. Distribution trends in the performance indicators

The distribution of the bioreactor performance indicators corroborates previous observations suggesting that the fermentation of H_2-rich gases may lead to higher productivity and gas utilization than the fermentation of CO-rich gases (Noorman and Heijnen, 2017) (Almeida et al., forthcoming) (see Figure 1). The observation is sustained on the fact that H_2 mass transfer to the liquid is faster than CO transfer; since mass transfer is linearly related for bioreactor productivity, then a higher mass transfer rate means higher productivity. Similarly, a higher productivity means than the gas consumption inside the bioreactor is more efficient, and therefore, gas utilization is higher.

Since BDS fermentation is simulated using the respective contributions of CO and H_2/CO_2 fermentations, then it is reasonable that bioreactor performance lies between the performances obtained for BOF offgas and H_2/CO_2 fermentations. In addition, as the H_2/CO ratio in the syngas is 2, then the performance of the syngas fermentor falls closer to that of the H_2/CO_2 fermentor than to the CO fermentor.

By comparing bioreactor performances with other study (Almeida et al., forthcoming) there is a high probability that gas utilization may be improved far more than bioreactor productivity. This observation is based on the fact that while the median gas utilization

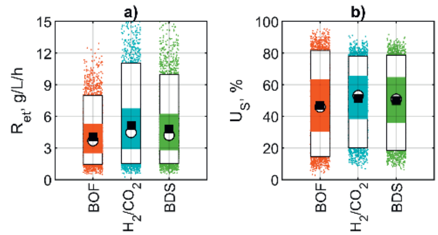

Figure 1 Boxplots summarizing the distribution of a) ethanol productivity and b) gas utilization. On the boxplots: the colored vertical rectangles represent the extension of the 25th and 75th percentiles; the white vertical rectangles represent the extension of the 5th and 95th percentiles; the small colored dots represent the outliers; the white circles represent the median values; and the black square boxes represent the mean values.

values are 45 and 53 % for CO and H_2/CO_2 fermentations, respectively, the median ethanol productivities are 3.7 and 4.5 g/h/L for CO and H_2/CO_2 fermentations, respectively. However, this observation does not necessarily suggest that productivity cannot be further increased, as there is a 25 % probability (see 25th and 75th percentiles in Figure 1) that R_{et} may increase to 5.3, 6.8 and 6.2 g/L/h for BOF offgas, H_2/CO_2 and BDS fermentations, respectively. In addition, there is a 5 % probability (see 5th and 95th percentiles in Figure 1) that R_{et} may be further improved to 8, 11 and 10 g/L/h for the same three gas supply options. That would be an improvement between 2 and 2.5 times from a previous report (Almeida et al., forthcoming).

Similarly, gas utilization in the bioreactor could be as high as 63, 66 and 65 % for BOF offgas, H_2/CO_2 and BDS fermentations, respectively with a 25 % probability. Gas utilization could climb to 82, 78 and 79 % for the same gas supply options with a 5 % probability. It is therefore, more probable that the BOF offgas fermentation case has a better gas utilization than the fermentation of H_2-rich gases.

In addition, although it may be encouraging to see that gas utilization could surpass 90 % as previously reported by LanzaTech, such achievement is highly unlikely with the proposed bioreactor configuration as there is only a 5 % probability that U_S may increase beyond 80 % (see Figure 1).

3.2. Sensitivity analysis by the standardized regression coefficients

Table 2 shows the standardized regression coefficients (β_{IP_i}) of ethanol volumetric productivity and gas utilization in the bioreactor. The value of R^2 is also included in Table 2 to show which OP's had an acceptable linear relation with all the IP's.

The relation between R_{et} and U_S and all the IP's is acceptably linear for the three gas supply cases. Remarkably, the IP's hierarchical classification is also common for these two OP's in three gas supply cases. Considering that the sign of the β_{IP_i} indicates whether the influence of each IP on one OP is positive or negative, R_{et} may be largely improved by p_t and the f_{k_La} and in a lower level of influence by the v_{sG}^c. On the other hand, the most detrimental IP for R_{et} is the gas feed dilution. According to [Almeida, forthcoming], these four IP's are deeply related to the rate of mass transfer in the bioreactor. f_{k_La} and ${v^c}_{sG}$ determine the value of the mass transfer coefficients while p_t and f_{Dil} determine the value of the partial pressures of the electron donors in the gas phase and therefore their saturation concentrations in the liquid phase and thus, their driving forces for mass transfer. While increases in p_t will widen the mass transfer driving force, increases in dilution will shrink the driving force.

Table 2 Standardized regression coefficients (β_{IP_i}) relating the model outputs with each input parameter

OP	**Gas supply case**	**IP**								R^2
		T	p_t	f_{Dil}	C_{et}^{max}	h_L	f_{k_La}	f_{Ac^-}	v_{sG}^c	
R_{et}	BOF	0.13	0.57	-0.36	0.02	0.14	0.54	-0.06	0.32	0.90
	H_2/CO_2	0.07	0.61	-0.43	0.00	0.07	0.45	-0.05	0.28	0.86
	BDS	0.09	0.60	-0.41	0.00	0.09	0.48	-0.05	0.29	0.88
U_S	BOF	0.18	-0.05	0.01	0.01	0.77	0.55	0.00	-0.13	0.95
	H_2/CO_2	0.11	0.15	-0.04	0.01	0.77	0.54	0.00	-0.13	0.92
	BDS	0.14	0.08	-0.02	0.01	0.78	0.55	0.00	-0.13	0.95

Gas utilization, in turn may be mostly improved by h_L, f_{k_La} and T, while v_{sG}^c will be slightly detrimental. The sensitivity of U_S to h_L is remarkably high as the β_{IP_i} is the closest to one, the maximum possible value. This relation is due to the fact that as the liquid column height increases, so does the residence time of the gas inside the bioreactor. On the other hand, v_{sG}^c offers the opposite effect: as the gas velocity through the bioreactor increases, the residence time decreases. In addition, the influence of f_{k_La} and T over U_S could be regarded as a side effect of their positive influence over R_{et}, which means that the mass transfer increases, the gas consumption is more efficient.

The influence of ethanol concentration over R_{et} and U_S is negligible according the estimated β_{IP_i}; the lack of mathematical connection between this IP and the two specified OP's (Almeida et al., forthcoming) might be the cause of this negligible influence of C_{et}^{max} over bioreactor performance. Thus, regarding the fact that possible inhibition by ethanol is not considered by the electron uptake kinetic expressions in the black-box model of microbial reactions, the negligible influence of C_{et}^{max} might be somewhat underestimated. The similarity between the sensitivities for the three gas supply cases is caused by the fact that the operation of the bioreactor does not differ significantly when either CO or H_2 are the electron donors (Almeida et al., forthcoming). However, the intensity of such sensitivities differ between the three cases. For example, BOF offgas fermentation R_{et} is the most benefited indicator when the mass transfer coefficient factor increases. Similarly, due to the inhibition of CO at high partial pressures, the bioreactor pressure has a negative effect over gas consumption in the BOF offgas case while pressure is mostly beneficial for the fermentation of H_2-rich gases.

4. Conclusions

The present study showed that ethanol volumetric productivity could be as high as 8, 11 and 10 g/L/h for the fermentation of BOF offgas, H_2/CO_2 and biomass-derived syngas, respectively. This increase may be achieved by a combination of high mass transfer coefficients, high top bioreactor pressure and large gas flow rates across the bioreactor.

These three IP's improve mass transfer rates and therefore ethanol productivity. In addition, the dilution of the gas feed is to be avoided since it has the most negative effect over productivity. The IP's that increase the productivity also have a positive impact on gas utilization. However, gas utilization may be mainly improved by tall bioreactors where the residence times are higher.

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