CHEMICAL ENGINEERING TRANSACTIONS
VOL. 37, 2014
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Eliseo Ranzi, Katharina Kohse- Höinghaus

ISBN 978-88-95608-28-0; **ISSN** 2283-9216
DOI: 10.3303/CET1437050

Simulation, Analysis and Optimization of an In Situ Gas Stripping Fermentation Process in a Laboratory Scale for Bioethanol Production

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The major problem associated with the bioconversion of ethanol for industrial fuel purposes is the ethanol inhibition in the fermentation process. One way to solve this problem is couple fermentation to a continuous product removal technique. The gas stripping *in situ* removal process has a number of advantages over other techniques, for example: it is simple, inexpensive to operate and do not harm the culture. In this work, the feasibility of *in situ* gas stripping fermentation process was studied using ASPEN PLUS® V.7.3. The process conditions were evaluated according to the existing laboratory scale design. The main process variables were investigated in order to achieve the best conditions to carry out an experimental plant, which is the planning of further work. The results show that such technique can lower ethanol concentration in a reactor making it below of inhibitory ranges. A correct choice of the optimized variables of the process provides a larger recovery of ethanol, contributing to the improvement and intensification of the fermentation process.

1. Introduction

Several geopolitical factors, aggravated by worries of global warming, have been fueling the search and production of renewable energy worldwide for the past few years. Such demand for renewable energy is likely to benefit the sugarcane ethanol industry in Brazil mostly because its energetic balance is positive and its price of production is relatively low. Brazil has several advantages in this scenario of biofuel production due to its expansive territory, geographical position, solar radiation, and abundant water resources. Besides, for more than 30 years the country has invested in improving the production of ethanol from sugarcane (Martinelli and Filoso, 2008).

Basically, the process for ethanol production from sugarcane is summarized in the extraction and conditioning of cane juice/molasses to make it assimilable to bioconversion in fermentation. The fermentation step is the central to the overall process for fuel ethanol production because it represents the transformation of sugar-containing raw materials into ethyl alcohol employing yeasts or other ethanol-producing microorganisms (Cardona et al., 2010).

Although being a crucial step for ethanol production, the alcoholic fermentation is characterized by high degree of inhibition due to ethanol concentration in broth. According to Maiorella et al. (1983), ethanol inhibition begins around 25 g/L and it is complete in 95 g/L. Thus, it is necessary to start with a relatively dilute glucose solution, usually not more than about 16 % by weight, in order to achieve complete conversion in a reasonable time (Taylor et. al, 1995). Another problem associated with the ethanol production for industrial fuel purposes, beyond ethanol inhibition of the fermentation step, is the high energy requested for product recovery. One way to solve these problems would be couple the fermentation process to a continuous product removal technique (*in situ* removals), so that inhibitory

Please cite this article as: Ponce G., Miranda J., Alves M., Wolf Maciel M.R., Maciel Filho R., Andrade R.R., Conto L.C., 2014, Simulation, analysis and optimization of an in situ gas stripping fermentation process in a laboratory scale for bioethanol production, Chemical Engineering Transactions, 37, 295-300 DOI: 10.3303/CET1437050

product concentrations are never reached. This would allow the use of concentrated substrate solutions, with a concomitant reduction in reactor volume, besides lesser dilution water would be added to the system, thus less energy would be requested (Maddox et al., 1995). The gas stripping *in situ* removal process has a number of advantages over other fermentation removal processes, for instance: it is simple, inexpensive to operate, does not harm the culture or suffer from fouling and clogging due to the presence of biomass like membrane use process, in the same way, none of expensive chemicals are used, just like liquid-liquid extraction technique (Ezeji et al., 2003).
The aim of this work is to investigate the best conditions to operate the gas stripping fermentation process in laboratory scale searching for high ethanol recovery and concentrations in the condensate, keeping the ethanol concentration as lower as possible in the broth. Based on these goals, the process simulation plays a crucial role during the analysis of technical feasibility of gas stripping process helping to guide the experimental trials.

2. Simulation of *in situ* gas stripping technique for bioethanol production

The fermentation process simulation with in situ gas stripping was carried out using the ASPEN PLUS® V.7.3. The bioconversion of sugars into ethanol takes place in the fermenter (represented in the simulation by a RSTOIC® block) continuously. The experimentally raw material used in laboratory is the sugarcane molasses, however, a simulation approximation was made to molasses being only glucose and water. The fermenter was modeled as experimentally determined conversions of specific reactions to *Saccharomyces cerevisiae* yeast based on industrial yields of sugarcane industries in Brazil. The assumption to simulate molasses as a glucose concentration greatly simplifies the stoichiometric equations used to simulate the fermentation process. Due to the lack of yeast compound and their properties in ASPEN PLUS®, it was necessary create it, in order to represent its cell growth reaction. The *Saccharomyces cerevisiae* yeast was included generically as a solid type with properties of component Zymo (Wooley and Putsche, 1996). In Table 1 are shown stoichiometric equations for products and cellular material production from glucose, as well as, the yield, according to Dias (2008).

Table 1: Conversion and Stoichiometric equations for product formation from glucose (Dias, 2008)

Product	Stoichiometric Reaction Equations	Yield (%)
Ethanol	$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$	90.48
Glycerol	$C_6H_{12}O_6 + 4H^+ \longrightarrow 2C_3H_8O_3$	2.67
Succinic Acid	$C_6H_{12}O_6 + 2H_2O \longrightarrow C_4H_6O_4 + 2CO_2 + 10H^+ + 10e^-$	0.29
Acetic Acid	$C_6H_{12}O_6 + 2H_2O \longrightarrow 2C_4H_4O_2 + 2CO_2 + 8H^+ + 8e^-$	1.19
Isoamilic Acohol	$C_6H_{12}O_6 \longrightarrow 0{,}8C_5H_{12}O + 2CO_2 + 0{,}15H^+ + 1{,}15H_2O + 15e^-$	3.1×10^{-4}
Yeast	$C_6H_{12}O_6 + 1.1429 \cdot NH_3 \longrightarrow 5{,}7143 \cdot Zymo + 0.2857 \cdot CO_2 + 2{,}57H_2O$	1.37

The description of the gas stripping fermentation process as well as the simulation approach follows just like in Van Der Merwe (2010) study. The flowsheet of the fermentation with *in situ* gas stripping is shown in Figure 1. The gas stripping process is simulated with a flash drum which is at the same conditions as the fermentation. Gas stripping process is not available at the conversion block (fermenter) in simulator, so an approximation for vapor-liquid equilibrium, which occurs originally in the reactor, should take place in a flash drum (flash separator type).The bottom product of the flash drum contains: water, excess nutrients, carboxylic acids, glycerol, not converted sugars, biomass and ethanol. This stream (A7) is centrifuged to separate biomass from the main broth. The biomass stream is recycled to the fermenter and the surplus biomass is purged from the process. The broth after centrifugation (stream R1), likewise is recycled to the first flash drum. A fraction of stream R1 is bled as the product of the fermentation process.
The top flash drum product, containing mostly ethanol, water and CO_2 gas, must be condensed and the remaining vapour stream (mainly CO_2) recycled. The condenser is simulated as a heat exchanger followed by flash drum to become easier the phase separation. Both condenser and flash drum are at the same conditions. A portion of the gas flow rate product (O2) is purged to obtain the remaining CO_2 flow rate as needed for gas stripping. The vapour stream (R4) has its pressure raised in a gas pump (compressor block) and then it is recycled to the gas stripping step. The amount of CO_2 produced during fermentation is

not the same amount bled per hour from the process, thus additional CO_2 need to be added in order to avoid gas accumulation in the system.

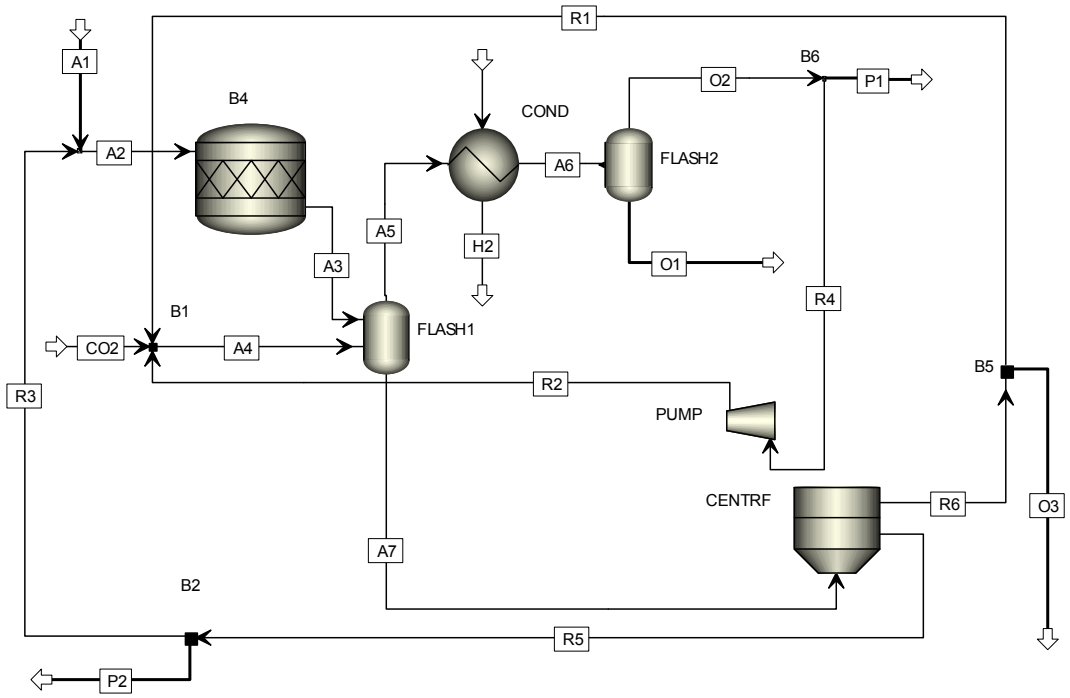

Figure 1: Flowsheet of continuous fermentation process with in situ gas stripping. Wider Lines Indicates stream inputs and outputs of the process

The non-random two-liquid activity coefficient model using the Hayden-O'Connell model for the vapour phase (NRTL-HOC) was used. NRTL model was chosen because its good performance to represent highly non-ideal mixtures. In the same way, the Hayden-O'Connell equation was chosen because it predicts dimerization in the vapour phase as occurs with mixtures containing carboxylic acids (acetic acid).The process also deals with CO_2 at temperatures above their critical temperatures. For ASPEN PLUS® correctly simulate this component, it is set to be Henry components (Van der Merwe, 2010).

3. Results and Discussion

Initially, it is presented a simulation case study of a gas stripping fermentation performed such as in laboratory scale. The simulation results of main streams (and components) for the process studied, are shown in Table 2 below:

Table 2: Stream data for Figure 1

Stream ID Stream	A1 Main Feed	A3 Reactor output	A4 Flash Feed	A5 Stripped Gas	A7 Stripped Broth	01 Cond.	03 Main Output	R2 Gas recycled
Temperature (K)	308.15	308.15	304.10	308.15	308.15	271.1	308.14	272.10
Vapor Fraction	0	0.055	0.083	1	0	0	1.44E-07	1
Mass Flow (Kg/hr)	0.126	0.127	3.992	0.689	3.429	0.023	0.089	0.638
Volume (L/min)	0.002	0.142	6.530	6.814	0.058	4.0E-04	0.001	5.331
Mass Fraction								
Glucose	0.25	0.009	0.011	3.11E-15	0.013	0	0.013	0
Water	0.75	0.753	0.754	0.023	0.901	0.620	0.901	0.001
Ethanol	-	0.111	0.056	0.016	0.066	0.338	0.066	0.004
Glycerol	-	0.006	0.007	1.74E-09	0.009	5.0E-08	0.009	1.22E-16
Acetic Acid	-	0.002	0.002	9.19E-06	0.002	2.0E-04	0.002	6.63E-08
CO_2	-	0.106	0.163	0.958	0.001	0.009	0.001	0.991

In this case, the fermentation was conducted continuously at 35 °C with a 0.639 kg/h (6 L/min) of CO_2 gas flow rate at -2 ºC of cooling temperature. The glucose concentration fed in the process was near to 25 wt%.

The results given in Table 2 show high ethanol concentration leaving the fermenter (A3 stream), with 11 % wt of ethanol. This concentration was decreased to 6.6 wt % (65 g/L) using the *in situ* gas stripping technique. Such technique allowed that the broth concentration remained under the complete inhibition concentration which is 95 g/ L of ethanol (Maiorella et al., 1983).

In this study, it was also observed that the percentage of ethanol continuously stripped in the fermenter (FLASH1 block) corresponded to 58 % of produced ethanol (stream A3). A percentual of 71 % of all ethanol stripped was condensate (stream A4 and A3), presenting an overall separation efficiency of 56.9 % (based on the ethanol produced in fermenter (stream A3)).

The results presented in Table 2 worked as guideline for sensitivity analyzes that were performed for the process variables: cooling temperature and gas flow rate. The analysis of cooling temperature was carried out for a 6 L/min of CO_2 permanent gas flow rate. The results of this analysis can be seen in Figure 2.

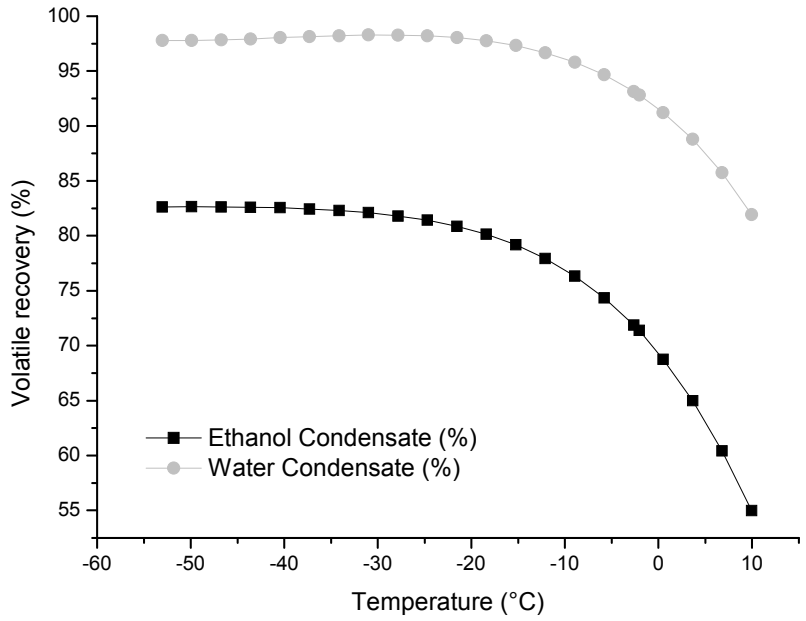

Figure 2: Relationship between the cooling temperature in condenser and the percentage of condensed volatile using CO_2 at 6 L/min gas flow rate

At the condensation temperature of 10 °C, only 55 % of ethanol entering the condenser is condensed. As the condensation temperatures decreases, the amount of ethanol condensed raises, respectively, with water condensation rising as well. The chart (Figure 2) shows that it is necessary a temperature lower than -20 °C to condense 80 % of ethanol, while at the same temperature over 95 % of water is condensed.

Analyzing these data, it was observed that complete condensation of ethanol from gas is not practical, since it will lead to complete condensation of water. Actually, temperatures below -5 ºC could hardly be applied in experimental trials due to current laboratory conditions in Brazil. According to Vane (2008), the heat of condensation of water per unit mass is 2.7 times that of ethanol, thus the evaporation and condensation of water in the system is critical to the overall energy efficiency of the process.

Regarding the gas flow rate, firstly, it is necessary to evaluate how it influences the decrease of ethanol concentration in the broth. The Ethanol concentration necessarily needs to be kept below the inhibitory concentration levels presented by Maiorela et al., (1983). In this way, the chart (Figure 3 below) presenting an analysis of how ethanol concentration in the broth varies due to the gas flow rate was carried out, taking into account: continuous fermentation at 35 ºC, glucose concentration near to 25 % wt, 6 L/ min CO_2 gas flow rate and -2 °C of cooling temperature in condenser.

After, on the same chart (chart of Figure 4), it is presented how the gas flow rate influences the behavior of the overall separation efficiency of ethanol and the ethanol concentration in the condensate. This evaluation is based on the same fermentation conditions mentioned above.

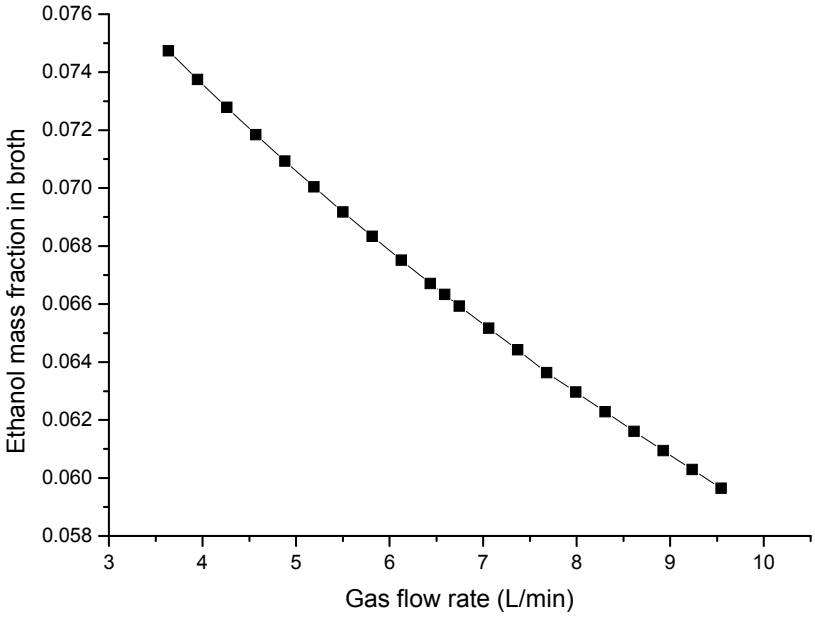

Figure 3: Ethanol concentration in the broth decreasing with the raise of the gas flow rate.

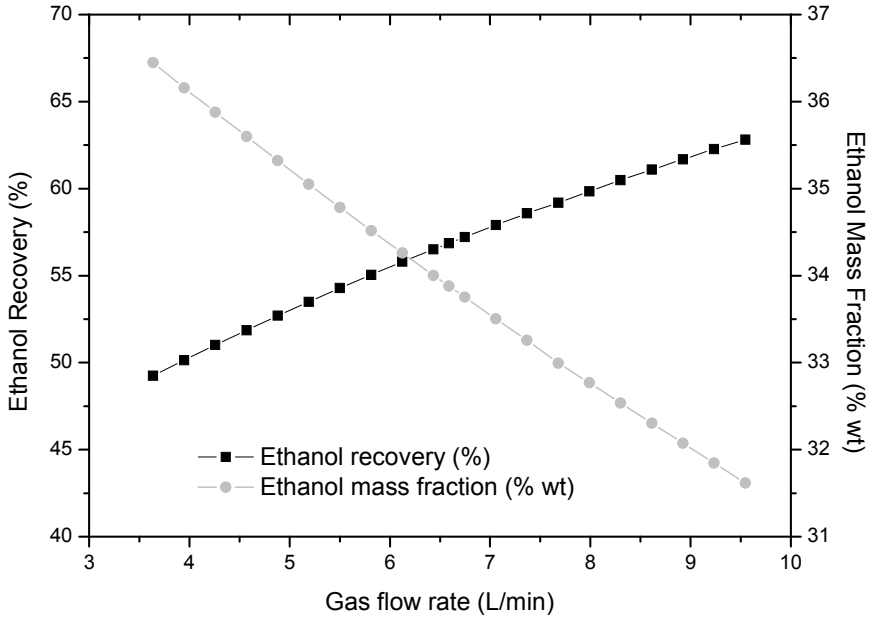

Figure 4: Influence of the gas flow rate on the behavior of the overall separation efficiency of ethanol (Ethanol Recovery) and the ethanol mass fraction in the condensate

From Figure 3, it is easily observed that the raise of the gas flow rate reduces the mass fraction of ethanol in the broth. Within the concentrations ranges studied, low gas flow rates are enough to decrease the ethanol concentration below the inhibition concentration limits.
From the data shown in Figure 4, it could be found that at high flow rates not only increased the ethanol removal, but also the water. The ethanol mass fraction in condensate is inversely proportional to the overall separation efficiency of ethanol. Thereby, to recover approximately 60 % of ethanol in the condensate stream (taking into account the ethanol produced in the fermenter), it is necessary a gas flow rate of 8 L/min. To this value of gas flow rate, the concentration in the broth corresponds to 6.3 % wt (61.5 g/L of ethanol) of ethanol and the ethanol concentration in the condensate corresponds to 33 % wt of ethanol. The condensed ethanol concentration should be specially considered because low concentrations in condensate raises the energy requested in the end-of-pipe alcohol recovery process (mainly distillation process), to produce ethanol in commercial concentrations.

4. Conclusions

A gas stripping fermentation process was evaluated through a case study based on real laboratory conditions. In this particular study, an amount of ethanol was continuously stripped from the fermenter (FLASH1 block) that corresponded to 58 % of ethanol. Therefore, even though the efficiency removal of ethanol be not complete, the percentage found is sufficient to decrease the concentration of ethanol significantly below the inhibitory effects caused thereby.
Low condensation temperature was found to have a positive effect in ethanol recovery and a negative effect on condensate concentration. The total water condensation negatively influences the process since a lot of energy is used for this purpose. Values among -2 to -5 ºC are interesting because it causes a substantial ethanol condensation and these values belong to the laboratory scale applicable ranges.
Concerning the gas flow rate, it is difficult to establish the best operating point or range to work with. High flow rate promotes higher ethanol removal in the system, improving overall separation efficiency, decreasing ethanol concentration in the broth. Nonetheless, negative impacts as the decrease of condensed ethanol concentration, was found. Thus, a balance between ethanol removal and end-of-pipe process energy usage is required, establishing a non-inhibitory concentration in the broth and an ideal concentration of ethanol in the condensate, making the process energy more attractive.

Acknowledgments

The authors are grateful to CNPq and FAPESP for the financial support.

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