A Strategy for Controlling Acetaldehyde Content in an Industrial Plant of Bioethanol

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Abstract: This work presents a strategy for controlling acetaldehyde content in Brazilian bioethanol, based in simulation results of a typical industrial distillation plant. The major problem of acetaldehyde in bioethanol is that, during the storage period, it can oxidize to acetic acid, increasing fuel acidity above the legislation limit. This work tested, by dynamic simulation, simple loops to control acetaldehyde in bioethanol. The dynamic simulation generated a disturbance in the wine to be distilled by increasing acetaldehyde content, and verified how those loops were able to control the acetaldehyde level in bioethanol. Two different column system configurations were investigated. The first one includes a degassing system and a second one that produces pasteurized alcohol without or with a degassing system. Suggestions for the best control system of acetaldehyde contamination in bioethanol were formulated according to the acetaldehyde level in the wine.

Keywords: Fuel ethanol, bioethanol, dynamic simulation, degassing system, aspen plus.

1. INTRODUCTION

There is an increasing interest in bioethanol as a renewable energy source as well as a commodity to be used in other industrial branches, such as the chemical, pharmaceutical, and beverage industries. Brazil is one of the largest bioethanol producers and the largest exporter. For more than 30 years bioethanol is used directly as a biofuel, in this case with a concentration close to the azeotropic one, or added to petrol and, in this last case, it should be anhydrous. The rapid increase in its use as biofuel, the increase of its exports and of its use in other industrial branches is requiring a better control of product quality. Several minor components are generated during bioethanol production by fermentation and most of them are contaminants present in the end product. Although ethanol distillation is a largely investigated subject, most of the research works focus on energy consumption, alternative dehydration techniques and control strategies for separating the binary mixture ethanol-water, not taking into account the series of minor components that influence the distillation process. Those research works also rarely consider the peculiarities of the column systems used for ethanol distillation in the industrial practice.

Some recent works are applying simulations tools in order to investigate spirits and bioethanol distillation, taking into account at least part of the complexity of the multicomponent alcoholic mixture and of the industrial equipments used for its distillation. GAISER et al. (2002) used the commercial software Aspen Plus for simulating a continuous industrial unit for whiskey distillation, validating the results against industrial data. MEIRELLES et al. (2008) simulated a continuous distillation column for spirits production from sugar cane fermented must. DECLOUX and COUSTEL (2005) simulated a typical distillation plant for neutral alcohol production, using the software ProSim Plus. Neutral alcohol is a very pure ethanol product that requires a series of distillation columns to be produced.

Taking into account the increasing importance of bioethanol and the largely untreated subject of controlling its contaminants, this work is focused on investigating strategies for controlling the acetaldehyde content in bioethanol. Acetaldehyde is the contaminant responsible for the increase in biofuel acidity during storage time.

2. DESCRIPTION OF PROCESS

A typical industrial installation for bioethanol production in Brazil, according to MARQUINI et al. (2008), is shown in Fig. 1. This industrial installation is composed by 3 columns, two stripping ones (A and B1) and the rectifying column B. Column A, a equipment for wine stripping, is composed by 22 plates, 1 reboiler and no condenser. These plates have Murphree efficiency of 0.65, the total pressure drop of this column is 18437 Pa, the pressure of stage 1 is 138932 Pa and the reboiler pressure 157369 Pa. The wine or beer, industrial denominations of the fermented sugar cane must, is represented by the standard solution given in Table 1. This mixture is fed into the top of column A. The stream named PHLEGM, a vapor stream with ethanol concentration within the range 35-45 mass%, is fed into the bottom of column B. STILLAGE and WHITE STILLAGE, streams withdrawn from the bottoms of columns A and B1, respectively, must have an ethanol content not larger than 0.02 mass%.

Column B, the phlegm rectification column, is composed by 45 plates plus a condenser, has Murphree efficiency of 0.50, a total pressure drop of 38932 Pa, condenser pressure of

100000 Pa and bottom stage pressure of 138932 Pa. Bioethanol is extracted as top product of column B with 93 mass% of ethanol. Column B1, the phlegm stripping column, is fed with the bottom product of column B. This column is composed by 18 plates plus a reboiler, has Murphree efficiency of 0.60, total pressure drop of 8042 Pa, and the reboiler pressure equal to 146974 Pa.

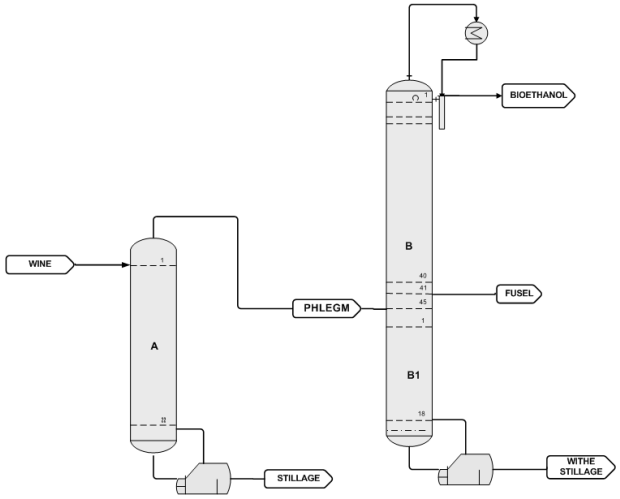

Fig. 1 - Brazilian Bioethanol Industrial Plant

Table 1. Typical composition of industrial wine used in the simulations.

Component	Concentration (mass fraction)	Reference
Water	0.93495357	By difference.
Ethanol	6.450×10^{-2}	Oliveira (2001)
Methanol	3.200×10^{-7}	Boscolo et al. (2000)
Isopropanol	1.020×10^{-6}	Cardoso et al. (2003)
Propanol	3.000×10^{-5}	Oliveira (2001)
Isobutanol	2.780×10^{-5}	Oliveira (2001)
Isoamyl alcohol	4.250×10^{-5}	Oliveira (2001)
Ethyl Acetate	7.690×10^{-6}	Oliveira (2001)
Acetaldehyde	2.000×10^{-6}	Oliveira (2001)
Acetic Acid	4.351×10^{-4}	Oliveira (2001)

3. MATERIALS AND METHOD

The first part of the present work focused on the steady-state simulation of a typical industrial unit, such as that shown in Fig. 1. The simulations were conducted using the commercial software Aspen Plus, by Aspen Tech, and aimed to investigate the operation of the industrial system by analyzing the effects of operational conditions upon the concentration profiles in columns A, B and B1. The second part was conducted using the module Aspen Dynamic, by Aspen Tech, so that some control strategies could be tested in order to keep the acetaldehyde level in bioethanol within the required limits. In this way the acidity increase of the biofuel during storage period could be prevented. The package RADFRAC for simulating distillation columns within Aspen Plus was selected in order to represent the whole industrial system. This package uses a rigorous method of calculation for solving the set of balance and equilibrium equations based on the MESH system described in detail by KISTER (1992). According to a detailed and rigorous analysis (Meirelles et al., 2008), previously performed for the vapor-liquid equilibrium of the binary mixtures formed by the wine components (Table 1), the NRTL model and a corresponding set of parameters were selected for representing the liquid phase non-ideality and the Virial equation, together with the approach based on HAYDEN-O'CONNELL (1975), for estimating the vapor phase fugacities.

Wine was fed into column A (see Fig. 1) with a mass flow of 202542 kg/h, at 94 ºC and the composition given in Table 1. The ethanol concentration in the bottom product of column A was fixed in 200 mg/kg (0.02 mass %) and the mass flow of bioethanol was varied around 14000 kg/h with at least 93 mass% of ethanol, corresponding to an approximately daily production of 465 m^3. In the bottom of column B1 the ethanol concentration was not fixed but it level was ever less than 200 mg/kg. In accordance with industrial information, the fusel stream mass flow was fixed in 41 kg/h, almost 0.3% of the bioethanol mass flow. Reflux and bioethanol stream mass flows were varied and the corresponding concentration profiles investigated.

For the dynamic simulation, in a first step a PID controller was used with the aim of controlling the acetaldehyde content (controller variable) in bioethanol, by manipulating the reflux stream and bioethanol mass flows (manipulated variables), after a perturbation in acetaldehyde concentration was imposed to the feed stream (wine). In a second step, the degassing system was tested to control the acetaldehyde content in bioethanol.

The degassing system is based on the association of two or more partial condensers in the top of column B. The vapor stream of each partial condenser is fed into the next one and the liquid streams return to the top of the column. In the last condenser, a small amount of vapor phase is withdrawn as a DEGASSING stream. According to the maximum level of allowed acetaldehyde contamination, the temperature of the last condenser can be varied and more or less mass of degassing can be generated.

4. RESULTS AND DISCUSSION

Almost all bioethanol fed into column A was stripped from the liquid phase and transferred via the PHLEGMA stream to column B. Except for acetic acid, all congeners (minor components in wine) are concentrated in the PHLEGMA stream and also transferred to column B. Fig. 2 shows the concentration profiles of water and ethanol along columns B (stages 1, condenser, to 46) and B1 (stages 47 to 65, reboiler). An alcoholic graduation of 93.0 mass% was obtained. Note that this value is within the concentration range required by the Brazilian legislation for hydrous bioethanol (Table 2).

Fig. 3 shows the concentration profiles for high alcohols. High alcohols, containing mainly isoamyl alcohol, are extracted from column B as a side stream named FUSEL stream.

Fig. 4 shows the concentration profile for acetaldehyde and acetic acid in columns B and B1. Acetaldehyde profile

indicates that this contaminant is concentrated in the biofuel stream.

ANP, the Brazilian National Petroleum Agency, is the public institution responsible for setting quality standards for fuels and biofuels. Copersucar, one of the largest Brazilian trading companies for sugar and bioethanol export, also sets specific quality standards according to the requirements of its clients. Table 2 shows the main specifications for bioethanol according to ANP (AEHC) and Copersucar (H1 and H2), and also some of the results obtained by steady-state simulation of the industrial plant (SIM). According to the simulation results the bioethanol produced fulfil the requirements of the Brazilian legislation and even most of the requirements set by Copersucar.

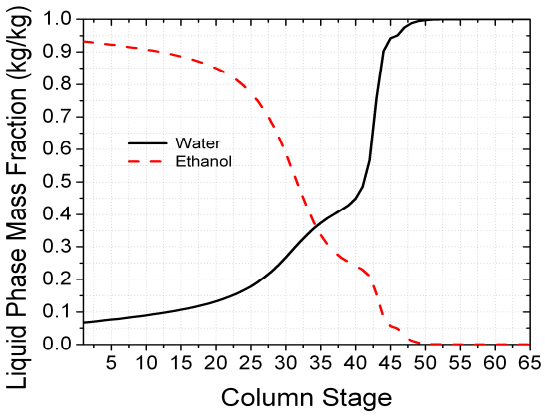

Fig. 2. Concentrations profile of ethanol and water in columns B (stages 1-46) and B1 (stages 47-65).

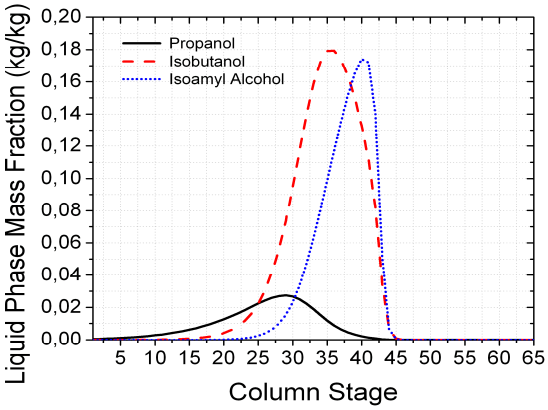

Fig. 3. High alcohols profiles in columns B (stages 1-46) and B1 (stages 47-65).

Acetaldehyde concentration is not a quality parameter fixed by ANP for the biofuel (Table 2). In case of the simulation results, the obtained acidity values, were far below the limit set by the Brazilian legislation. However, during the storage period acetaldehyde can oxidize to acetic acid and deteriorate the biofuel quality, increasing its acidity. If all acetaldehyde content present in the simulated fuel ethanol (Table 2) oxidizes to acetic acid, the product acidity would be increased to 33.5 mg/L. With this value, the biofuel would be outside the standards qualities established by the Brazilian legislation (Table 2). For this reason, the concentration of acetaldehyde in biofusel must be strictly controlled to prevent that the acidity level exceeds the legislation limits along the storage time. On the other hand, Brazil is nowadays the largest bioethanol exporter and the use of this bioproduct is increasing worldwide not only as an alternative energy source as well as an input material for chemical, pharmaceutical, perfume and beverage industries. Although these other uses may require further purification steps, sometimes conducted at the importing country, the Brazilian exporters are opting for defining stricter quality standards, such as the values specified by Copersucar (see Table 2). This highlights the importance of monitoring and controlling the contamination levels of minor components, such as acetaldehyde and high alcohols, in bioethanol.

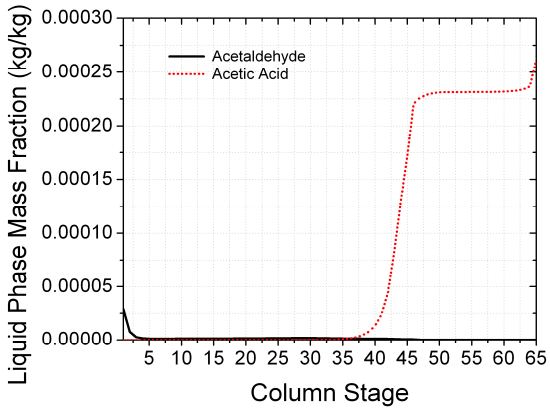

Fig. 4. Acetaldehyde and acetic acid profiles in columns B (stage 1-46) and B1 (stages 47-65)

Table 2. Bioethanol quality standards, ANP (AEHC), Copersucar (H1 and H2) and the simulation results (SIM).

Spec.	Unities	Bioethanol			
		AEHC	H1	H2	SIM
Alcoholic Graduation	mass%	92.6-93.8	≥ 92.8	≥ 93.8	93.2
Acidity (Acetic Ac.)	mg/L	≤ 30	≤ 20	≤ 10	Trace
Density (20ºC)	kg/m^3	807.6-811.0	-	-	807.1
Acetaldehyde	mg/L	-	≤ 50	≤ 10	24.6
High Alcohols	mg/L	-	≤ 400	≤ 50	332.5

Data on the mechanism and kinetics of acetaldehyde oxidation to acetic acid can be found in WANG et al. (1992) and XU et al. (2000). In order to avoid the risk of this oxidation during biofuel storage one of the possible strategies is to reduce acetaldehyde content in biofuel to a minimal value. In the second part of this work, some strategies to control the acetaldehyde content were investigated. All the strategies were based in a PID loop control, with the aim of keeping acetaldehyde concentration in bioethanol constant even if a perturbation increases its content in the wine. Figure 5 shows the simplest configuration of column simulated in the present work. As acetaldehyde is a very light component, the total amount of this substance present in the wine will

contaminate bioethanol if this configuration is used. For this reason no control strategy would be able to avoid an increase of acetaldehyde contamination in bioethanol in case of a slight increase in its concentration in the wine. In fact, attempts to avoid this contamination, by using reflux and/or bioethanol flow, according to the loop control represented in Fig. 5, failed. Thus two alternative solutions are suggested and they include changes in the industrial installation.

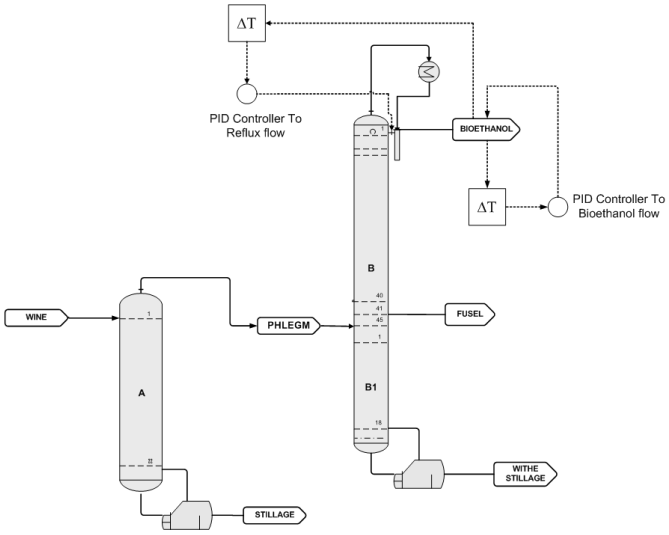

Fig. 5. Loop control for acetaldehyde concentration in bioethanol

The first alternative installation includes a degassing system, as that shown in Fig. 6 and explained above. Such a system makes easier the control of acetaldehyde content in bioethanol. As a very light component, acetaldehyde concentrates in the vapor streams and is eliminated by the DEGASSING stream. Controlling the DEGASSING flow makes possible to eliminate part of the acetaldehyde contamination, although this also causes small losses of the bioproduct.

Fig. 7 shows steady-state results for DEGASSING flow, ethanol mass flow in degassing and acetaldehyde content in bioethanol as a function of the last condenser temperature. The increase of this temperature increases the degassing flow, and by consequence increases the mass flow of ethanol in degassing stream, and decreases the acetaldehyde concentration in the bioethanol. These results show that the control of the temperature of the last condenser in the degassing system can control the concentration of acetaldehyde in the bioethanol. Taking this into account, a simple PID controller was developed to control the temperature of the last condenser of the degassing system (see Fig. 6). In this loop control, the controller variable was the acetaldehyde content in bioethanol and the manipulated variable was the temperature of the last condenser. The stack point (maximum level of the acetaldehyde in bioethanol) was fixed in 25.3 ppm (2.530×10^{-5} kg/kg). With this concentration, even if all the acetaldehyde oxidize to acetic acid, the mass of acid formed will not be sufficient to exceed the acidity maximum level fixed by ANP (Table 2). In order to better represent the industrial process, carbon dioxide (CO_2) produced during fermentation was included in the wine composition in a concentration of 0.0011 kg/kg. This value was determined assuming that the alcoholic fermentation industrial process is performed in closed vat with light over pressure (600 to 800 mm of water) and temperatures close to 35 °C. Considering that gas phase inside the vat is composed of saturated CO_2 with vapors of ethanol and water, the NRTL model and the Henry constant for CO_2 (Dalmolin et al., 2006) was used in order to estimate the solubility of CO_2 in the wine. The estimated values varied within the range 1050 to 1150 mg/kg. The acetaldehyde concentration in the wine was increased to 2.100×10^{-6} kg/kg and after 3 hours decreased to 1.900×10^{-6} kg/kg, in order to demonstrate the efficiency of the degassing system. The concentration of the other wine components were kept constant in the values indicated in Table 1, except for water whose value was appropriately adjusted. The results are present in the Fig. 8.

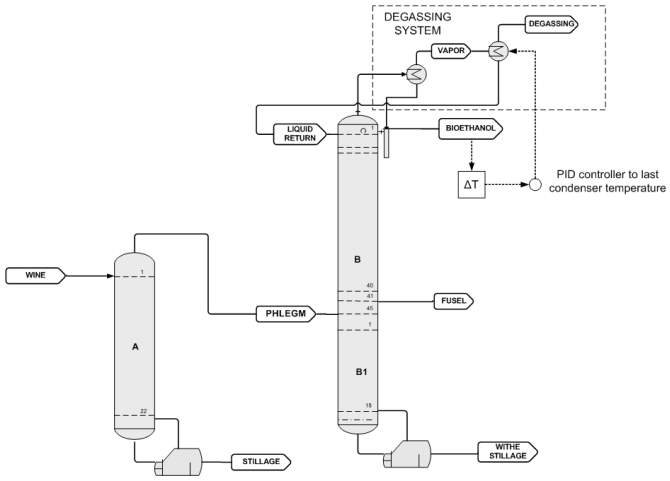

Fig. 6. Industrial plant with degassing system

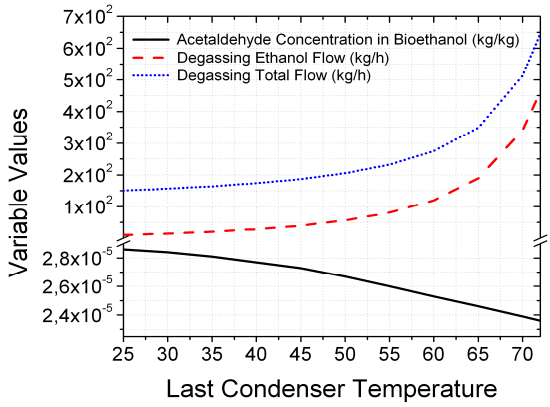

Fig. 7. Acetaldehyde content and degassing flow as a function of last condenser temperature

As is possible to observe in Fig. 8, the control system based in a PID controller has a good performance in avoiding a contamination of acetaldehyde in bioethanol. A direct dependence between the controller variable (biofuel acetaldehyde concentration) and the manipulated variable (last condenser temperature) was observed. In case of an

increase of acetaldehyde concentration in the wine the PID controller increases the last condenser temperature and, in consequence, a large degassing flow is withdrawn of the equipment. The acetaldehyde level in bioethanol reaches safe values after 40 minutes and stabilizes after one hour. The reverse process occurs when the concentration of acetaldehyde in wine is decreased (see Fig. 8).

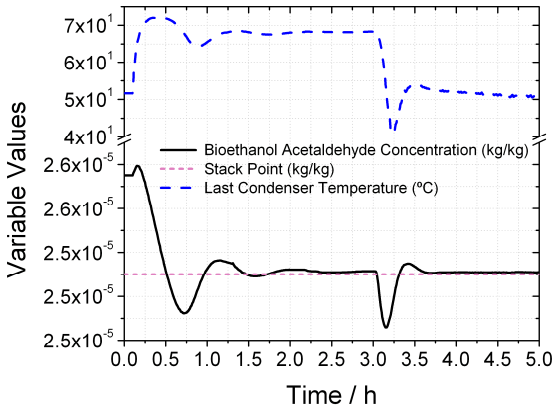

Fig. 8. Results of PID controller in degassing system (industrial installation)

Despite this good performance, the configuration with a degassing system may exhibit some difficulties in case of a large wine contamination with acetaldehyde. Large concentrations of acetaldehyde in wine require larger flow of degassing stream in order to reduce the biofuel contamination. A larger degassing mass flow increases ethanol losses (see Fig. 7). Therefore, the total loss of the ethanol in the production system can reach levels higher than those accepted by industry. An alternative configuration better for a wine with larger acetaldehyde contamination is the pasteurized bioethanol installation shown in Fig. 9. In this kind of installation two news columns (D and A1) are added to the original system. These columns concentrate the major part of wine volatile compounds, including acetaldehyde, and eliminate part of them via the SECOND ALCOHOL stream withdrawn from the top of column D.

In column B bioethanol is withdrawn from a tray close to the column top. In the top of Column B a further SECOND ALCOHOL stream is also withdrawn. According to Fig. 4 acetaldehyde is concentrated in the trays located close to the top of column B. For this reason streams such as the two SECOND ALCOHOL ones are concentrated in acetaldehyde and other light minor components, for instance ethyl acetate. These contaminants are taken away by the top streams and bioethanol, withdrawn from column B as a side stream, has its acetaldehyde content decreased. On the other hand, small amounts of ethanol are not recovered as the main product (bioethanol), being extracted in those byproduct streams. Such scheme is more appropriate for producing bioethanol from a wine with larger contamination of light components or in case the bioproduct must have a higher purity.

Fig. 10 shows the results of steady state simulations performed for the pasteurized bioethanol installation. For this simulation acetaldehyde concentration in the wine was increased to approximately 10 times the value of the previous simulations (new concentration equal to 1.900×10^{-5} kg/kg), representing a larger contamination, closer to the industrial wine, according to Oliveira (2001).

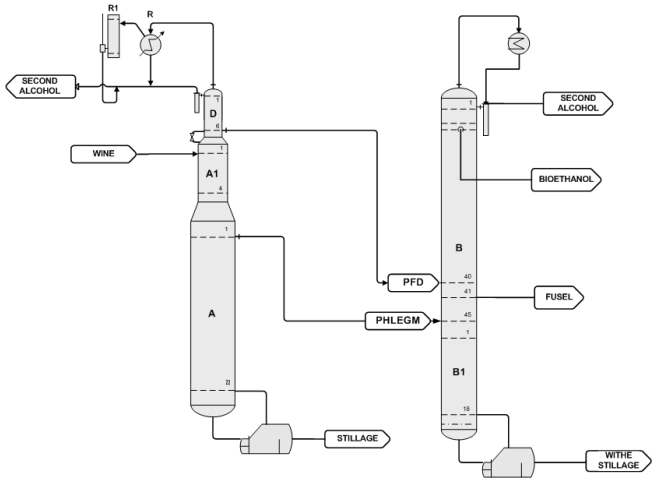

Fig. 9. Industrial plant for bioethanol with second alcohol streams.

The main objective of those simulations was to show that, varying the mass flow of the second alcohol stream in column B, it is possible to reduce considerably the concentration of acetaldehyde in bioethanol. According to Fig. 10, the increase of the mass flow of the second alcohol stream reduces acetaldehyde contamination without influencing, in a significant way, the bioproduct alcoholic graduation. In these simulations only the second alcohol stream in top of column B was varied, keeping the second alcohol stream in top of column D fixed at the value 400 kg/h.

This means that a relative larger acetaldehyde contamination is contained in the second alcohol stream, a result that makes easier the control of this contamination in the main product (pasteurized bioethanol) by means of the degassing system. For this reason a loop control similar to that of Fig. 6, connecting the acetaldehyde concentration in pasteurized bioethanol (controller variable) to the last condenser temperature (manipulated variable), was tested. The wine acetaldehyde concentration was increased to 2.000×10^{-5} kg/kg and the last partial condenser temperature was varied to stabilize the bioethanol acetaldehyde concentration at 2.450×10^{-5} kg/kg. With this value, the problem of acetaldehyde oxidation during storage time was eliminated. The result of this simulation was presented in Fig. 11.

The results show that in almost 2 hours the acetaldehyde concentration reaches the required value although the stabilisation time is approximately 7 hours. This result suggests that the degassing system is an excellent alternative for acetaldehyde control in bioethanol, provided that the wine contamination with acetaldehyde is not too large.

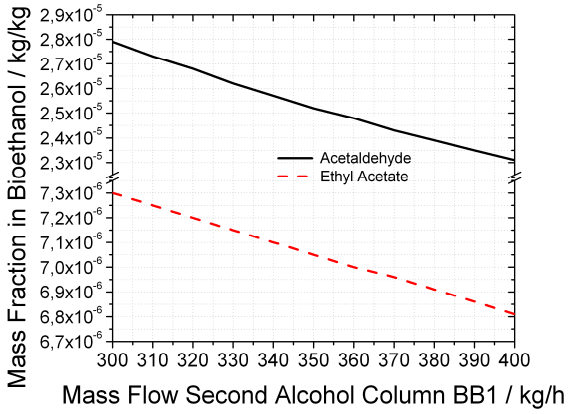

Fig. 10. Volatiles content in bioethanol in function of second alcohol flow of column BB1

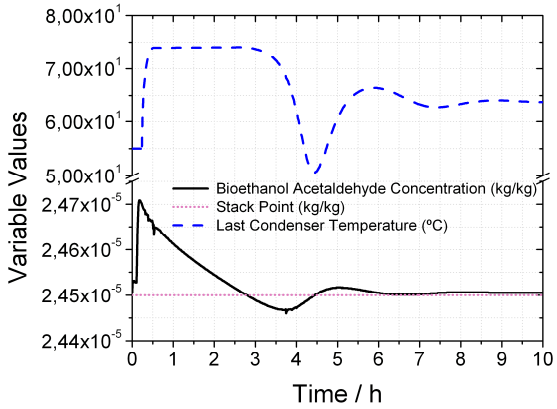

Fig. 11. Results of PID controller in degassing system (pasteurized bioethanol installation)

5. CONCLUSION

Production of bioethanol as a renewable fuel or as an input commodity to be used in other industrial branches requires the reduction and control of several contaminants contained in the fermented must. In the present work special attention was focused on controlling acetaldehyde contamination. Analyzing the results presented it is possible to conclude that the wine (must) acetaldehyde concentration will determine the type of industrial installation and the type of control to be used to regulate the acetaldehyde in bioethanol and prevent problems with its oxidation during storage. Thus, for wine with less than 2.0×10^{-6} kg/kg of acetaldehyde, the industrial installation without degassing system is appropriate. For wine concentrations within the range 2.0×10^{-6} to 2.2×10^{-6} kg/kg, the degassing system is required. In case of wine concentrations within the range 2.2×10^{-6} to 2.0×10^{-5} kg/kg, the pasteurized bioethanol installation is the most appropriate one. For concentrations within the range 2.0×10^{-5} to 2.2×10^{-5} kg/kg the degassing system should be included in the pasteurized bioethanol installation. Finally, for musts with higher acetaldehyde concentration ($\geq 2.2\times10^{-5}$ kg/kg) the pasteurized bioethanol installation with a PID controller to regulate the mass flow of second alcohol is probably the best way to prevent problems with acetaldehyde oxidation during storage.

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