Computer simulation applied to studying continuous spirit distillation and product quality control

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**A R T I C L E   I N F O**

Article history:
Received 7 June 2010
Received in revised form 2 March 2011
Accepted 8 March 2011

Keywords:
Spirits
Distillation
Simulation
Aspen Plus
Degassing
Bioethanol

**A B S T R A C T**

This work aims to study continuous spirit distillation by computational simulation, presenting some strategies of process control to regulate the volatile content. The commercial simulator Aspen (Plus and dynamics) was selected. A standard solution containing ethanol, water and 10 minor components represented the wine to be distilled. A careful investigation of the vapor–liquid equilibrium was performed for the simulation of two different industrial plants. The simulation procedure was validated against experimental results collected from an industrial plant for bioethanol distillation. The simulations were conducted with and without the presence of a degassing system, in order to evaluate the efficiency of this system in the control of the volatile content. To improve the efficiency of the degassing system, a control loop based on a feedback controller was developed. The results showed that reflux ratio and product flow rate have an important influence on the spirit composition. High reflux ratios and spirit flow rates allow for better control of spirit contamination. As an alternative to control the volatile contents, the degassing system was highly efficient in the case of low contamination. For a wine with high volatile contamination, the pasteurized spirit distillation unit was the best alternative.

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**1. Introduction**

Spirits are produced by fermentation and distillation of different raw materials in many places around the world. Examples include *Whisky*, a typical UK spirit (Scotland, Ireland) produced by distillation of fermented grain mash and aged in wooden casks (*Gaiser, Bell, & Lim, 2002; Piggott, Conner, Paterson, & Clyne, 1993; Suomalainen, Nykanen, & Eriksson, 1974*), *Rum*, a typical Caribbean drink produced by distillation of sugar cane molasses and aged in oak barrels (*Da Porto & Soldera, 2008; Pino, 2007*), *Vodka*, a typical Russian beverage obtained by distillation of alimentary ethanol from grain or potato fermented must, usually distilled to higher alcohol graduation and afterwards diluted (*Login, Rudnitskaya, Seleznev, & Vlasov, 2005; Savchuk, Kolesov, & Nuzhnuy, 2007*) and *Cachaça* (*cacha*-sa), a typical Brazilian spirit produced by the distillation of fermented sugar cane juice, with an alcoholic graduation within the range of 38–54% by volume (*Brazil, 2005; Cardoso, Lima-Neto, Franco, & Nascimento, 2003; Scanavini et al., 2010*).

In general, the main differences between these spirits are the alcoholic graduation and the concentration of the congeners (minor compounds) in the beverage, as shown in Table 1. Usually these congeners, present in low concentrations (10^{-6}–10^{-4} mg/L) in the fermented must and in the beverage, are responsible for characterize each type of spirit (*Valderrama, Huerta, & Alarc, 2002*). The main congeners produced during fermentation are alcohols (methanol, propanol, and isoamyl alcohol), organic acids (acetic acid), carbonyl compounds (acetaldehyde) and esters (ethyl acetate) (*Lurton, Snakkers, Roulland, & Galí, 1995*). Table 1 shows some quality standards for different spirit beverages produced around the world according to their respective country legislation. In the case of aged spirits the alcohol content by volume of the distillate is higher, for instance: aged cachaça, distilled to 75 °GL and whisky distilled to 93–96 °GL. After aging the spirit is diluted to the desired alcohol graduation.

Carbonyl compounds are responsible for the most volatile aroma fraction of alcoholic beverages. The presence of these compounds is highly desirable but if their concentration is very high, the quality of the spirits is diminished and some problems for the health of consumers are generated (*Nykänen, 1986*). One of these problems is the “hangover” syndrome caused by high levels of acetaldehyde (*Nascimento, Cardoso, Neto, & Franco, 1998*);

Ethanol is the predominant alcohol found in spirit beverages and is responsible for their body. Higher alcohols, such as isoamyl alcohol, isobutanol, propanol and isopropanol, are the main group responsible for the spirit flavor. Isoamyl alcohol typically represents...
half the amount of higher alcohols (Oliveira, 2001). Propanol concentration is usually low in high quality spirits (Nykänen, 1986). Methanol is another alcohol that requires strict control since high ingestions of this compound can cause severe intoxication (Paine & Dayan, 2001).

The complexity of the fermented must makes it difficult to study the spirit distillation process. Nowadays computational simulators are able to accurately represent the most complex industrial processes. Using the commercial software PRO/II, Haypek et al. (2000) simulated an industrial plant for distilling aroma processes. Using the commercial software PRO/II, Haypek et al. are able to accurately represent the most complex industrial spirit distillation process. Nowadays computational simulators and the simulated results showed good agreement with the consumer expectations in the spirit. On the other hand, in higher concentrations they can reduce the commercial value and cause harm to the consumer’s health.

A typical industrial installation for continuous cachaça distillation is presented in Fig. 1. The distillation column has a small rectifying section, composed of 2 or 3 trays, and a stripping section composed of 16–18 trays. No side stream for removal of higher alcohols (propanol, isopropanol, isobutanol and isoamyl alcohol) is necessary and normally a small reflux ratio is required for attaining the product specifications. Almost all ethanol fed to the column is recovered in the distillate stream. The bottom product should have a maximum ethanol content around 0.02% in mass, which corresponds to a loss of approximately 0.3 to 0.6% of the total ethanol fed to the distillation equipment.

Control of the volatile content (aldehydes, methanol, ketones and esters) present in the spirit is a very important factor in regards to product quality and food safety for consumers, because of the association of these components to special beverage sensorial characteristics and some diseases (Nascimento et al., 1998; Nykänen, 1986). Changes in the equipment configuration are

### Table 1
Quality standards of different spirits beverages.

<table>
<thead>
<tr>
<th>Component</th>
<th>Cachaça&lt;sup&gt;a&lt;/sup&gt; (Brazil)</th>
<th>Tequila&lt;sup&gt;b&lt;/sup&gt; (Mexico)</th>
<th>Rum&lt;sup&gt;b&lt;/sup&gt; (Ecuador)</th>
<th>Aguardiente&lt;sup&gt;b&lt;/sup&gt; (Spain)</th>
<th>Regular&lt;sup&gt;b&lt;/sup&gt; (Eurasia)</th>
<th>Vodka&lt;sup&gt;b&lt;/sup&gt; (Ukraine)</th>
<th>Whisky&lt;sup&gt;b&lt;/sup&gt; (Eurasia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol Graduation (GL)</td>
<td>38–54</td>
<td>38–55</td>
<td>35–48</td>
<td>79.5</td>
<td>38–40</td>
<td>40–50</td>
<td></td>
</tr>
<tr>
<td>Volatile acidity, in acetate (mg/100 ml anhydrous ethanol)</td>
<td>0–150</td>
<td>0–100</td>
<td>0–100</td>
<td>0–100</td>
<td>0–100</td>
<td>0–18</td>
<td>5–70</td>
</tr>
<tr>
<td>Acid, in ethyl acetate (mg/100 ml anhydrous ethanol)</td>
<td>0–200</td>
<td>2–270</td>
<td>0–100</td>
<td>0–100</td>
<td>0–100</td>
<td>0–18</td>
<td>5–70</td>
</tr>
<tr>
<td>Aldehydes, in acetaldehyde (mg/100 ml anhydrous ethanol)</td>
<td>0–30</td>
<td>0–40</td>
<td>0–20</td>
<td>0–20</td>
<td>0–3</td>
<td>2–12</td>
<td></td>
</tr>
<tr>
<td>Superior Alcohols (mg/100 ml anhydrous ethanol)</td>
<td>0–360</td>
<td>20–400</td>
<td>0–150</td>
<td>0–900</td>
<td>0–2</td>
<td>50–250</td>
<td></td>
</tr>
<tr>
<td>Methanol (mg/100 ml anhydrous ethanol)</td>
<td>0–20</td>
<td>30–300</td>
<td>0–10</td>
<td>0–80</td>
<td>0.03% (v/v)</td>
<td>0–15</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Brazil (2005); <sup>b</sup> Distill (2007).

<table>
<thead>
<tr>
<th>Component</th>
<th>Boiling point (°C)</th>
<th>Concentration range (w/v)</th>
<th>Reference</th>
<th>Fixed value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100.0</td>
<td>0.92–0.95</td>
<td>By difference</td>
<td>0.932000</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78.40</td>
<td>0.05–0.08</td>
<td>Oliveira (2001)</td>
<td>0.066150</td>
</tr>
<tr>
<td>Methanol</td>
<td>64.70</td>
<td>0.0–3.0 × 10⁻⁸</td>
<td>Boscolo, Bezzera, Cardoso, Neto, and Franco (2000)</td>
<td>3.200 × 10⁻⁷</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>82.40</td>
<td>1.020 × 10⁻⁶</td>
<td>Cardoso et al. (2003)</td>
<td>1.020 × 10⁻⁶</td>
</tr>
<tr>
<td>Propanol</td>
<td>97.10</td>
<td>2.1–6.8 × 10⁻⁵</td>
<td>Oliveira (2001)</td>
<td>3.360 × 10⁻⁵</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>108.00</td>
<td>1.3–4.9 × 10⁻⁵</td>
<td>Oliveira (2001)</td>
<td>2.780 × 10⁻⁵</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>132.00</td>
<td>2.7–18.8 × 10⁻⁵</td>
<td>Oliveira (2001)</td>
<td>1.425 × 10⁻⁴</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>77.10</td>
<td>5.5–11.9 × 10⁻⁶</td>
<td>Oliveira (2001)</td>
<td>7.690 × 10⁻⁶</td>
</tr>
<tr>
<td>Acetatehydroxide</td>
<td>20.20</td>
<td>1.0–8.3 × 10⁻⁵</td>
<td>Oliveira (2001)</td>
<td>1.580 × 10⁻⁵</td>
</tr>
<tr>
<td>Acetone</td>
<td>56.53</td>
<td>3.3–99.3 × 10⁻⁴</td>
<td>Estimated</td>
<td>1.500 × 10⁻⁵</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>118.10</td>
<td>4.351 × 10⁻⁴</td>
<td>Oliveira (2001)</td>
<td>4.351 × 10⁻⁴</td>
</tr>
<tr>
<td>CO₂</td>
<td>–78.00</td>
<td>1.100 × 10⁻³</td>
<td>Estimated</td>
<td>1.100 × 10⁻³</td>
</tr>
</tbody>
</table>
sometimes required in order to control the volatile concentration in the beverage. One of these changes is the inclusion of a degassing system as indicated in Fig. 1 by the dashed line. This system is based on the association of two or more partial condensers at the top of the column. The vapor stream of each partial condenser is fed into the next condenser and the liquid streams return to the top of the column. In the last condenser, a small portion of the vapor phase is withdrawn as a degassing stream. According to the volatile concentration of the spirit, the temperature of the last condenser can be varied to generate a larger or smaller degassing stream, decreasing the volatile concentration in the spirit. Since it is used only for product quality control, the degassing flow rate is always very low in order to avoid significant ethanol losses.

Most of the research on spirit's production reported in the literature is focused on the sensorial quality of the beverage (Ledauphin, Basset, Cohen, Payot, & Barillier, 2006; Madera, Lobo, & Alonso, 2010; Piggott et al., 1993; Soufliros, Mygdalia, & Natskoulis, 2004), but recently a modest effort has been undertaken to evaluate the influence of the distillation process on product quality. Taking this into account, the present work used the computational simulation to investigate the continuous distillation of a standard solution containing ethanol, water and ten minor compounds, aiming to improve the performance of a typical industrial plant for continuous cachaça production. One of these changes is the inclusion of a degassing loop suggested for maintaining volatile components within the quality requirements for the final product.

2. Material and methods

2.1. Vapor–liquid equilibrium

The complexity of the fermented must, due to its multicomponent composition and low concentration of congeners, makes difficult accurate prediction of the vapor–liquid equilibrium and it can be considered the main source of errors in the simulation of distillation processes (Faúndez & Valderrama, 2004). Taking this into account, the first step of this work was to thoroughly investigate the vapor–liquid equilibrium of the alcoholic wine.

The vapor-liquid equilibrium is given by the equality of fugacities in both phases, as described in Eq. (1) (Prausnitz et al., 1980; Sandler, 1999).

\[ \phi_i y_i P = \gamma_i x_i P_{vi} \]  

(1)

Where, \( y_i \) is the molar fraction of component \( i \) in the vapor phase, \( P \) is the total pressure of the system, \( \gamma_i \) is the activity coefficient of component \( i \) in the liquid phase, \( x_i \) is the molar fraction of component \( i \) in the liquid phase, \( P_{vi} \) is the vapor pressure of component \( i \) at the system temperature, and \( \phi_i \) the fugacity coefficient of component \( i \) in the vapor phase.

In the present case the NRTL model was chosen for calculating the activity coefficients (\( \gamma_i \)) and the Virial equation, with the Hayden and O’Connell (1975) model, was used to estimate the fugacity coefficients.

In order to check and eventually improve the representation of the vapor–liquid equilibrium (VLE) the following procedure was used. Experimental data for binary mixtures containing wine components (see Table 2) were collected from literature sources (Bernetová, Aim, & Wichterle, 2006; DAvila & Silva, 1970; Freshwater & Pike, 1967; Gmehling & Onken, 1981; Murti & Van Winkle, 1958; Ortega & Hernández, 1999; Resa, González, Moradillo, & Ruiz, 1997). From 66 binary mixtures required for describing the wine VLE, experimental data were available for 43 mixtures. In such cases the equilibrium was calculated using the NRTL interaction parameters available in the Aspen Plus databank and compared with the experimental data. When the average absolute deviation (\( \Delta y_i \)) between experimental and calculated data was larger than 0.03, the NRTL parameters were readjusted on the basis of the corresponding experimental data. The above indicated deviations were calculated according to Eq. (2) below:

\[ \Delta y_i = \frac{\sum (y_{\text{Experimental}} - y_{\text{Calculated}})}{n} \]  

(2)

Where \( y \) is the vapor phase concentration and \( n \) is the number of experimental points for the binary mixture.

For the others 23 binary mixtures without any reported experimental data available in literature, the Aspen Plus NRTL parameters were used since they were already available in the software databank or could be estimated using the UNIFAC group contribution method. These estimated parameters included all binary mixtures with CO2 and some others, such as acetaldehyde/iso-butanol, acetone/isoamyl alcohol, and acetic acid/isoamyl alcohol.

Carbon dioxide is produced during fermentation and may have an important impact on the wine vapor—liquid equilibrium. In order to estimate its concentration in the wine it should be considered that industrial fermentation is conducted in closed vessels under a light over pressure (gauge pressure of 600–800 mm of water column) and temperature near 32 °C. Assuming that the gas phase inside the vessel is composed of carbon dioxide saturated with water and ethanol vapors, the carbon dioxide solubility in a wine with 8 °GL was estimated as varying within the range of 1050–1100 mg CO2/kg of wine. These estimated values were based on the NRTL model for
ethanol—water mixtures and the Henry constants reported by Dalmolin et al. (2006) for CO₂ dissolved in hydroalcoholic solutions. An average value of 1100 mg CO₂/kg of wine was selected for the wine composition (see Table 2).

Using the selected NRTL parameters, the relative volatilities for wine components \( \alpha_{jk} \) were calculated according to Eq. (3).

\[
\alpha_{jk} = \frac{y_j/x_j}{y_k/x_k} = \frac{\gamma_j p^{pp}}{\gamma_k p^{pp}} \frac{\phi_j}{\phi_k}
\]

(3)

Where \( \alpha_{jk} \) is the relative volatility of component \( j \) in relation to \( k \), \( x \) is the liquid phase concentration, \( \gamma \) is the liquid phase activity coefficient, \( \phi \) is the vapor phase fugacity coefficient and \( p^{pp} \) is the vapor pressure.

In order to obtain a better insight on the behaviors of the different congeners during alcoholic distillation, the relative volatilities of these compounds were calculated with the Aspen Plus simulator, using an isobaric flash drum at 1 atm. The congeners were always assumed to be at very low concentrations (mass fractions between \( 10^{-4} \) and \( 10^{-5} \)) and the ethanol concentration of the hydroalcoholic solution fed into the flash drum varied along the entire range of mass fractions (\( 10^{-4} \)–0.99). According to the observed behaviors the congeners could be classified as light components when presenting volatility greater than ethanol, intermediate volatility compounds when their volatilities are greater than water but lower than ethanol and heavy components when they have volatility lower than water.

2.2. Validation of the process simulation

In order to check whether the results generated by computational simulation are reliable, an experimental validation of the process simulation was conducted, comparing the obtained results with the information collected in an industrial plant. For this purpose experimental samples and data were collected from the industrial plant of Santa Adélia Mill, located in Jaboticabal town, State of São Paulo, Brazil. This industrial plant produces 300 m³ of anhydrous cachaça production, the validation of the process simulation focused on the correct description of this stripping unit. For this purpose some sampling points were installed in tray 17 (T17), corresponding to the bottom of column A1, tray 16 (T16), corresponding to the top of column A, and tray 10 (T10). Samples of wine, phlegm and stillage were also collected. All samples were analyzed by gas chromatography (GC), as described below. Additional information about the temperatures of trays 16 and 1 (stillage withdrawal) was also acquired as well as information about the temperature and flow rate of the input stream. Using the input information mentioned above a static simulation was conducted with the Aspen Plus simulator and the simulated results compared with the experimental compositions and temperatures of those selected trays and output streams.

2.2.1. GC analysis

All the samples collected were filtered on filter paper with 0.2 μm of porosity. After clarification, the samples of trays T17, T16, T10 and of phlegm were weighed in glass flasks of 5 ml, and diluted with Milli-Q water (Millipore) using a ratio of 40 mg of original sample to 1 ml of final mixture. For samples of stillage and wine, by virtue of its low components concentration, the dilution ratio was adjusted to approximately 100 mg of original sample to 1 ml of final mixture.

The GC analysis was performed in a Capillary Gas Chromatograph model Shimadzu 6850 SERIES equipped with an autosampler and with a flame ionization detector (FID). The components of the liquid samples were separated in a column DB-624 crosslinked (6% cyanopropyl-phenyl 94% dimethylpolysiloxane) with dimensions of 60 m of length, 0.25 mm of internal diameter and 1.4 μm of film thickness. After several tests, the best column operational conditions was determined as follows: pressure column of 215 kPa (isobaric); injector and detector temperature was fixed at 210 °C; the volume of sample injection was set at 1.5 μl with a split ratio of 1:30; the flow of carrier gas (helium) in the column was set at 2.4 ml/min with a linear velocity of 35 cm/s; the temperature gradient started at 40 °C (4 min); 1 °C/min until 80 °C; 10 °C/min until 180 °C, staying at this temperature for five minutes.

The components were quantified by the external standard technique through the combination of calibration curves to eleven components. All standard components were chromatographic grade produced by Sigma Aldrich, with purity >99.9%. Calibration curves were constructed using eight points, analyzed in triplicate, for the following components and their respective range concentrations: Acetaldehyde (1220–0.3 mg/l), Methanol (1100–0.3 mg/l), Ethanol (41,000–0.2 mg/l), Acetone (800–0.3 mg/l), Isopropyl alcohol (1000–0.3 mg/l), Propanol (3500–0.3 mg/l), Ethyl Acetate (1000–0.3 mg/l), Isobutanol (3600–0.3 mg/l), Acetic Acid (500–0.3 mg/l) and Isosamyl Alcohol (7500–0.3 mg/l). It was observed that all components produced identifiable peaks when their concentrations were higher than 0.1 mg/l (0.000001 in mass fraction), being this value fixed as a lower detection limit. The composition of the industrial wine was used as the feed stream for the simulation run performed for validation purpose. In case of minor components not identified during the wine GC analyses, their composition in the feed stream was fixed at the minimum chromatography detection limit value. Its occurs, for instance, for isopropyl alcohol. The mass fraction of water was quantified by difference.

2.3. Simulation of spirit production

Static simulations were conducted with the Aspen Plus simulator, using the RADFRAC package. This package uses the MESH equations (Kister, 1992) for rigorously calculating distillation columns. Initially, an industrial plant without degassing system
(see Fig. 1) was investigated. The distillation column has 23 stages, including reboiler and condenser, and the tray efficiency was fixed at 0.7 (70%). Wine was fed at stage 4 (numbered from top to bottom) with mass flow of 10,000 kg/h and temperature of 97°C. The distillation column has 23 stages, including reboiler and condenser, and the tray efficiency was fixed at 0.7 (70%). Wine was fed at stage 4 (numbered from top to bottom) with mass flow of 10,000 kg/h and temperature of 97°C. The wine composition is given in Table 2. Column top and bottom pressures were fixed at 100 kPa and 137.4 kPa, respectively. The spirit mass flow and reflux ratio were varied from 1000 to 2000 kg/h and 0.001 to 1.5, respectively. In sequence, the degassing system was included and strategies for controlling the spirit volatile content were investigated. Acetaldehyde and ethyl acetate concentrations in wine were increased to 26 mg/kg and 175 mg/kg, respectively, in order to generate the risk that their concentrations in cachaça may be outside the range of values fixed by the Brazilian legislation (see Table 1). The temperature of the final condenser in the degassing system was varied from 25 to 75°C in order to produce a larger or smaller degassing flow rate, expressed as a spirit (distillate) percentage, so that its influence on spirit volatile content, spirit alcohol graduation and ethanol losses in the degassing stream could be investigated. Furthermore, a control loop based on feedback control (PID) was developed using Aspen Dynamics. The temperature of the final condenser was manipulated in order to control spirit’s volatile content. The control loop response was tested via a disturbance in the wine acetaldehyde and ethyl acetate concentrations. Finally, a distillation column configuration based on the work of Whitby (1992) and presented by Gaiser et al. (2002) was tested. This column, shown in Fig. 2, is a typical industrial installation for whisky production. It has 35 stages in the rectifier section and 27 stages in the beer striper. Spirit is withdrawn from stage 8 (from the top) and fusel oils (higher alcohol) from stage 33. Ethanol is separated from fusel oil in a simple side column with 10 plates, where the aqueous phase is withdrawn from the top and the organic phase from the bottom. At the top of the main column, a small stream (called second alcohol stream), rich in volatile compounds, was withdrawn. The liquid phase from the degassing system is recycled to the first tray of the main column, and the aqueous phase from fusel oil side stream is pumped back to the feed to the main column. This configuration is particularly appropriate for producing spirits with high alcohol graduation, mainly those submitted to an aging process, such as whisky and aged cachaça. In the present study this system was named pasteurized spirit distillation unit.

2.4. Sensitivity analysis to the NRTL binary interaction parameters

Aiming to verify the sensitivity of the distillation process state variables in relation to the NRTL binary interaction parameters, a sensitivity analysis was performed taking into account a fermented must containing water, ethanol and one congener of each component class mentioned before, i.e. light components (Acetaldehyde), intermediate volatility compounds (Isoamyl Alcohol) and heavy components (Acetic Acid). To perform this sensitivity analysis some simulations were conducted with the same operational conditions presented in the Spirits Production topic above and with the wine containing ethanol and the three minor components indicated before with the same concentrations shown in Table 2. In these simulations a change of ±5% in the values of the NRTL binary interaction parameters was considered. The liquid phase mass fractions of those components in all column trays and the temperature of these trays were compared to the simulation results performed with the NRTL original parameters. An absolute deviation, calculated in relation to the values obtained with the NRTL original parameters, was obtained following Eq. (4) below.

$$
\varepsilon = \frac{1}{n} \sum |S_0 - S_1|
$$

Where $\varepsilon$ is the deviation value, $S_0$ is the value of the distillation process state variable (compositions or temperatures) obtained with the NRTL original binary parameters, $S_1$ is the value of state variable obtained taking into account a change of ±5% in the NRTL parameters and $n$ is the number of column trays.

3. Results and discussion

3.1. Vapor–liquid equilibrium

For calculating the vapor phase non-ideality, the Virial equation of state coupled with the Hayden and O’Connell (1975) model was used.
used. This approach is the most appropriate, especially in the case of binary mixtures containing acetic acid, since this organic compound dimerizes in the vapor phase.

In the case of activity coefficients calculated by the NRTL equation, interaction parameters were readjusted for 33 binary mixtures from the set of 43 mixtures with experimental data available in literature. Before readjustment, the average absolute deviation for the vapor phase molar fraction was 0.0130 (maximum of 0.0570). After the necessary readjustment, the average absolute deviation was reduced to 0.0085 (maximum of 0.0282). In the case of equilibrium temperature, the average absolute deviation was 0.78 °C (maximum of 2.53 °C) before readjustment and 0.40 °C (maximum 1.72 °C) after. As shown by the results, the new NRTL interaction parameters could significantly reduce the deviations in the phase equilibrium calculations, a result that contributes to a more reliable process simulation.

Fig. 3a presents the relative volatility of the light elements in relation to water for different ethanol mass fractions in the liquid phase. These light elements are generally represented by aldehydes (acetaldehyde), ketones (acetone) and esters (ethyl acetate). As can be observed, the relative volatilities of light components decreases steadily as the ethanol concentration in the mixture increases, but their values are always greater than one. This means that these components tend to be concentrated in the vapor phase. Fig. 3b presents the relative volatility of ethanol and methanol, two light elements, and acetic acid, a heavy element, in relation to water. Methanol is more volatile than water along the entire concentration range, but ethanol volatility approaches one for concentrations within the mass fraction range of 0.9–1.0, because of the azeotropic behavior of ethanol-water mixtures. Based on Fig. 3a and b it is possible to conclude that acetaldehyde, acetone and ethyl acetate are more volatile than ethanol for the whole range of concentrations. Because of this characteristic, these components tend to concentrate at the top of the column, significantly affecting spirit quality. Methanol has a volatility relatively close to that of ethanol, showing values slightly lower in the ethanol diluted region (ethanol mass fraction in liquid phase lower than 0.47) and slightly higher in the ethanol concentrated region. This occurs because the larger ethanol activity coefficient in the diluted region compensates the larger values of methanol vapor pressure. In any case, methanol-ethanol separation is difficult since their relative volatility is small and they tend to exhibit a similar distillation behavior. Fortunately, methanol concentration in wine is usually very low, except when sources of methoxilated pectins are added to the must before fermentation (Meirelles et al., 2009: chap. 3). The volatility of acetic acid is always lower than water and ethanol (see Fig. 3b), so this component concentrates in the column bottom and is mostly eliminated in the stillage (vinasse).

Fig. 3c and d shows the relative volatility of the higher alcohols in relation to water. These components exhibit a decrease in volatility as the ethanol concentration in the liquid phase increases, acting as light components in the ethanol diluted range and as heavy components in the ethanol concentrated range. Because of this behavior they should be classified as components with intermediate volatility. Although the higher alcohols present vapor pressures always lower than the corresponding values for ethanol, they are more volatile than ethyl alcohol in the ethanol diluted concentration range because their activity coefficients in aqueous solutions tend to be very large. As the ethanol concentration in the liquid phase increases, these activity coefficients decrease steadily and the same occurs for their volatilities.

### 3.2. Validation of process simulation

As mentioned above, the samples from the industrial plant for alcohol distillation were analyzed by GC. Linear calibration curves were obtained for all standards with high values of determination coefficients ($R^2$), always higher than 0.992. Aiming to verify the reproducibility of the calibration curves two different solutions, containing water, methanol, ethanol, propanol, acetic acid and isoamyl alcohol at known concentrations, were analyzed by GC. A maximum deviation between the value obtained by the GC analysis and the original composition of the above mentioned mixtures was obtained for acetic acid and this deviation has a value of 15%. A higher deviation was expected in case of acetic acid because the selected chromatographic column is not so appropriate for analysis.
of organic acids due to its relatively low polarity. This column was selected because it is the most appropriate for ethanol and for all other minor compounds. For this reason the deviations for other components were much lower, with a maximum value of 5.5% and an average value of 2.5%. Such results indicate a very good quality of components were much lower, with a maximum value of 5.5% and other minor compounds. For this reason the deviations for other components were much lower, with a maximum value of 5.5% and an average value of 2.5%. Such results indicate a very good quality of components were much lower, with a maximum value of 5.5% and an average value of 2.5%. Such results indicate a very good quality of components.

The comparison of the experimental compositions of the experimental samples analyzed by GC and the simulated results was performed in terms of the mass fractions of water, ethanol and of the minor components as a group, as well as in terms of the temperatures measured in an industrial plant for bioethanol distillation. For the congeners, represented in Table 3 as a group of components, the experimental and the corresponding simulated values always have the same order of magnitude, even in the case of very low experimental mass fractions, such as the value observed in tray T10 (0.000023). Nevertheless, the relative deviations are higher, attaining values around 30% in case of trays T25, T17 and T16. Table 4 gives the complete experimental and simulated compositions for the phlegm and stillage stream. As can be seen, the experimental and simulated results for all minor components have the same order of magnitude, although the deviations are high, in relative terms.

Considering all the results obtained in this validation test it is possible to conclude that, for the major components and for temperatures, the simulation results are correct from a qualitative as well as a quantitative point of view. In case of the minor components, process simulation should be considered as able to provide good qualitative results that reproduce correctly the major trends of their distillation behavior, but does not give low deviations in relation to the experimental values. However, it should be noted that for all components with mass fraction below the chromatography detection limit, with the exception of isopropyl alcohol, the simulated results are below $10^{-9}$ or $10^{-10}$. Furthermore, it should be considered that isopropyl alcohol was not detected in the industrial wine and, in fact, one does not know whether this component is not present in the wine or its composition is below the minimum GC detection limit. Taking into account that the experimental and simulated results for all minor components have the same order of magnitude, the simulation results can be considered as a reliable estimate of their distillation behavior and of its dependence on the operational conditions and equipment design.

3.3. Simulation of spirit production

Fig. 4a gives the spirit alcohol content by volume as a function of product flow rate and reflux ratio (RR). For low reflux ratios, in some cases very low ratios, such as $RR = 0.001$, the alcoholic graduation is relatively low but larger than the minimum value required by the legislation for Brazilian cachaça (38 °GL, see Table 1). For lower spirit flow rates, the reflux ratio must be increased in order to avoid larger losses of ethanol in the stillage, as can be seen in Fig. 4b. From a industrial point of view these ethanol losses should be no larger than 0.6% of the ethyl alcohol amount fed into the column (see the short dash dot horizontal line in Fig. 4b), corresponding to a maximum ethanol concentration of 200 mg/kg in the stillage. Larger reflux ratios increase the spirit alcoholic graduation (see Fig. 4a), in some cases to concentrations much greater than the maximum required by legislation (54 °GL for cachaça). Greater alcohol graduations are sometimes required, either by legislation or for improving the beverage aging process. Whisky (Gaiser et al., 2002; Suomalainen et al., 1974), Absinthe (Lachenmeier, 2007) and Vodka (Legín et al., 2005; Savchuk et al., 2007), by virtue of their specific legislation, should be distilled to higher alcohol graduations and later diluted to acceptable levels for human consumption (see Table 1). In case of Brazilian cachaça, only the aged spirit is distilled to higher alcohol graduations and diluted after the aging process. For this investigation (feed stream of 10,000 kg/h with 8.5 °GL), cachaça flow rates and reflux ratios varying from 1000 to 2000 kg/h and 0.001 to 1.5, respectively, allow for spirit production with an alcohol graduation within the appropriate concentration range (38–54 °GL, see Table 1). The industrial plant shown in Fig. 1 is not appropriate for distilling spirits to high alcoholic graduations, for instance to 96 °GL. In such case, the pasteurized spirit distillation unit (see Fig. 2) is recommended and some results for this type of industrial unit will be discussed later.

Fig. 5 shows the concentration of volatile congeners, represented by acetaldehyde, in alcoholic beverages. As can be observed, low acetaldehyde contaminations are obtained only by using large spirit flow rates or by combining low spirit flow rates with large reflux ratios. A similar behavior was also observed for other volatile compounds, but the component concentration range depends on the

### Table 3

Simulated and experimental values (compositions in mass fractions).

<table>
<thead>
<tr>
<th>Component</th>
<th>Phlegm</th>
<th>Stillage</th>
<th>Phlegm</th>
<th>Stillage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.057516</td>
<td>0.941822</td>
<td>0.000662</td>
<td>–</td>
</tr>
<tr>
<td>T25</td>
<td>0.524082</td>
<td>0.465191</td>
<td>0.010727</td>
<td>–</td>
</tr>
<tr>
<td>T23</td>
<td>0.457914</td>
<td>0.530161</td>
<td>0.011125</td>
<td>–</td>
</tr>
<tr>
<td>T17</td>
<td>0.064354</td>
<td>0.935112</td>
<td>0.000534</td>
<td>–</td>
</tr>
<tr>
<td>T16</td>
<td>0.042423</td>
<td>0.957302</td>
<td>0.000275</td>
<td>104.0</td>
</tr>
<tr>
<td>T10</td>
<td>0.004125</td>
<td>0.959652</td>
<td>0.000023</td>
<td>–</td>
</tr>
<tr>
<td>Stillage</td>
<td>0.0000353</td>
<td>0.999326</td>
<td>0.000101</td>
<td>103.0</td>
</tr>
<tr>
<td>Phlegm</td>
<td>0.283419</td>
<td>0.714623</td>
<td>0.001958</td>
<td>104.0</td>
</tr>
<tr>
<td>–</td>
<td>0.286600</td>
<td>0.717175</td>
<td>0.001685</td>
<td>103.0</td>
</tr>
</tbody>
</table>

### Table 4

Experimental and simulated compositions for Phlegm and Stillage.

<table>
<thead>
<tr>
<th>Component</th>
<th>Phlegm</th>
<th>Stillage</th>
<th>Phlegm</th>
<th>Stillage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>DL</td>
<td>1.12 × 10⁻⁸</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0000499</td>
<td>0.0000802</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.2834743</td>
<td>0.2866373</td>
<td>0.0003636</td>
<td>8.540 × 10⁻⁸</td>
</tr>
<tr>
<td>Acetone</td>
<td>DL</td>
<td>0.0000003</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>DL</td>
<td>0.0000535</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Propanol</td>
<td>0.0005359</td>
<td>0.000588</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.000221</td>
<td>0.000117</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>0.0004423</td>
<td>0.0002741</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>DL</td>
<td>2.394 × 10⁻⁸</td>
<td>0.0002761</td>
<td>0.000267</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>0.0009259</td>
<td>0.0008423</td>
<td>DL</td>
<td>Trace</td>
</tr>
<tr>
<td>Water</td>
<td>0.7146496</td>
<td>0.7171416</td>
<td>0.9913094</td>
<td>0.999733</td>
</tr>
</tbody>
</table>

a DL – Minimum detection limit for the GC analyses (10⁻⁸ mg/mg).

b Trace ≤ 10⁻⁸ mg/mg (Aspen Technology, 2003).
specific component. In the case of ethyl acetate, the concentration range in spirits varies from 9.2 to 17.8 mg/100 ml anhydrous ethanol (AE) for the same range of operational conditions. The corresponding range of values for acetone is from 17.9 to 33.3 mg/100 ml AE. As shown in Table 1, congener concentrations are usually evaluated in mg of the component by ml of AE contained in the spirit. For acetaldehyde, the range of values obtained in the simulations, 19.0–34.0 mg/100 ml AE, corresponds to the range from 6.8 mg/100 ml of spirit (79.0 mg/kg spirit) to 12.8 mg/100 ml of spirit (158.0 mg/kg spirit). Both graphs in Fig. 5 represent the same simulation results, but the units of concentration used in Fig. 5b (mg/kg of spirit) make it clear that the reflux ratio has only a very slight influence on the acetaldehyde content of the spirit. This is also true for other congeners, such as ethyl acetate and acetone. In fact, this behavior points out that the effect of reflux ratio observed in Fig. 5a is due to the use of concentrations expressed in mg of congeners/ml of AE, since the reflux ratio has a large influence on the spirit alcohol graduation (Fig. 4a).

As previously mentioned, control of the volatile content is important for the spirit quality. According to Table 1, this is especially true for whisky and vodka, beverages that require a more strict control of the volatile content. In this case, the use of the degassing system and/or a more complex configuration of the distillation unit is recommended.

Another important congener class is represented by the higher alcohols, composed mainly of isoamyl alcohol (over 60% of the total quantity of higher alcohols). Fig. 6 shows that their concentrations in the spirit, expressed in mg of congeners/100 ml of AE and mg of congeners/kg of spirit, increase for low spirit flow rates and low reflux ratios.

Spirit acidity as a function of the product mass flow and reflux ratio shows a somewhat different behavior (see Fig. 7). Since acetic

Fig. 4. Spirit alcohol graduation (a) and ethanol loss (b) as a function of spirit mass flow and reflux ratio (RR).

Fig. 5. Spirit acetaldehyde concentration as a function of spirit mass flow and reflux ratio (RR).
Acid is a heavy component, its concentration in the beverage decreases as the reflux ratio is increased, an effect that is to some extent, mitigated by the increase of the product mass flow.

Based on the prior simulation results, a specific set of operational conditions (spirit mass flow = 1500 kg/h and reflux ratio = 0.5) was selected in order to investigate the performance of a degassing system included in the equipment configuration, as indicated by the dashed line in Fig. 1. The levels of acetaldehyde and ethyl acetate in the wine were increased to 26 mg/kg and 175 mg/kg, respectively, so that a spirit produced without the degassing system would be outside of legislation limits.

Alcoholic fermentation is an anaerobic process that generates a relatively large concentration of carbon dioxide in the wine. As an extremely light component, its presence in the top product can be easily decreased by the degassing system, with the further advantage that it also facilitates control of the other volatile congeners in the spirit.

Fig. 6. Total higher alcohols in spirits as function of spirit mass flow and reflux ratio (RR).

![Fig. 6](image_url)

Fig. 7. Spirit acidity as function of spirit mass flow and reflux ratio (RR).

![Fig. 7](image_url)

Fig. 8 presents the influence of the degassing system on the spirit alcohol graduation and ethanol loss. The increase in temperature of the final condenser raises the ethanol loss in the degassing system and slightly decreases the spirit alcohol graduation. The main component in the degassing stream is carbon dioxide, but most of the light components fed into the column are withdrawn in this stream (see Fig. 9) and small amounts of ethanol are lost. In the case of Brazilian cachaça, a final condenser temperature of 55 °C, representing a degassing ratio of 0.6% (3 kg/h of degassing stream) and an ethanol loss of 0.35%, is sufficient to meet the limits specified by legislation for acetaldehyde and ethyl acetate.

A control loop for the final condenser temperature, based on a PID controller, makes it possible to avoid that any disturbance in acetaldehyde and ethyl acetate concentration in the wine compromises their concentration in the product. Fig. 10 shows the results for this control system simulated by Aspen Dynamics.
perturbation caused in the wine concentration, increasing acetaldehyde and ethyl acetate concentration in a unique step from 26 to 30 mg/kg and 175 to 200 mg/kg, respectively, was easily stabilized by the control loop based on the final condenser temperature.

Unfortunately, perturbations larger than those investigated above cannot be controlled using only a degassing system. In the case of acetaldehyde and ethyl acetate concentrations greater than 30 mg/kg and 200 mg/kg respectively, the final condenser temperature would be so large that the degassing stream would correspond to almost the entire vapor stream fed into the last condenser. This indicates that this kind of system is efficient for controlling volatile concentration only within a restrict range of wine contamination.

In fact, in some spirits the limits of volatile content are so strict and the alcoholic graduation so high that a modification in the configuration of the distillation unit is required. For these beverages the industrial plant presented in Fig. 2 is the best option. In order to test the efficiency of this configuration, a simulation was performed with a wine having the same composition shown in Table 2.

The simulation results show a spirit with the following characteristics: 96 °GL, 0.13 mg of acetaldehyde/100 ml of AE, 0.64 mg of ethyl acetate/100 ml of AE, 1.03 mg of total higher alcohols/100 ml of AE and 0.26 mg of methanol/100 ml of AE. This spirit is in accordance with the standards set for whisky (see Table 1). On the other hand, the distillation unit shown in Fig. 2 is able to produce spirits with different standards by simply adjusting the operational conditions. For beverages whose allowable content of minor components is larger, the following operational conditions can be used: lower reflux ratios, higher spirit flow rates and no withdrawal of the second alcohol and fusel oil streams. This leads to energy saving and minimal ethanol loss. In the case of beverages that are submitted to a more strict concentration standard for minor components, higher reflux ratios and lower spirit flow rates are required and the second alcohol and fusel oil streams must be withdrawn.

Aiming to investigate the influence of the second alcohol stream on the spirit volatile concentration, a series of static simulations was performed while maintaining constant the acetaldehyde and ethyl acetate concentrations in the wine (26 mg/kg and 175 mg/kg respectively) and the degassing flow rate (0.6% of spirit flow rate).

Fig. 11 shows that the increase of the second alcohol stream can reduce spirit volatile contamination. On the other hand, the spirit alcoholic graduation decreases only slightly until the second alcohol...
stream reaches 60 kg/h (4% of the spirits flow rate) and then shows a steep decrease for greater flow rates of this byproduct. This indicates that, for spirits that require high alcohol graduation (vodka and whisky) and are obtained from wines with high volatile contaminations, a larger ethanol loss from the second alcohol stream will be necessary in order to promote the volatile control in the spirits. In the particular case simulated in the present work, a flow rate of 45 kg/h for the second alcohol stream is sufficient to stabilize the spirit ethyl acetate concentration at 18 mg/100 ml AE and to produce a beverage according to the quality standards required for vodka and whisky (see Table 1). In case of acetaldehyde, it is possible to produce a spirit according to legislation for all values of second alcohol flow rate (30–100 kg/h) investigated in the present study. These results suggest that a control loop to manipulate the second alcohol flow rate may be a good option to maintain spirit volatile contents within the required limits.

3.4. Sensitivity analysis of process simulation results to the NRTL binary interaction parameters

Table 5 shows the results for the sensitivity analysis of the process state variables in relation to the NRTL binary interaction parameters. These deviations were calculated according to Eq. (4) and represent average absolute differences between the simulated results obtained with the original set of parameters and those obtained after a change of ±5% in their values.

Taking into account the compositions observed along the entire column, Table 4 indicates that the average absolute deviations for the major components, ethanol and water, was less than 0.002 in mass fraction. In case of the minor components these average differences have values always lower than 0.000005, also in mass fraction. The absolute differences are a little bit higher in case of the spirit composition, 0.0062 for the major components and lower than 0.000025 for the minor components, but even in relative terms these differences are not large. For instance, a maximum difference of 1.4% was obtained for spirit alcoholic graduation, indicating a small variation of its composition. For the minor components the relative differences in spirit composition were always lower than 2.7%, suggesting that also in this case the change in the parameters did not have a large effect.

For the temperature, the average absolute deviation was not higher than 0.39 °C, a value that corresponds to a relative deviation of 0.40%. In case of steam consumption, a variable very important for evaluating the energy performance of continuous distillation, the absolute deviation was less than $7.5 \times 10^{-4}$ kg of steam per liter of spirit, representing a relative deviation of 0.08%.

The results presented above suggest that the changes considered in the set of NRTL parameters used in the present work do not have a large impact on product quality, tray temperatures and energy performance of the equipment, indicating that process simulation based on these parameters can be a powerful and reliable tool for evaluating the effects of variations in the operational conditions and in the design of equipments for spirit distillation.

Nevertheless, such results should not be overestimated. The original set of parameters used in the present work was thoroughly readjusted in order to better describe the phase equilibrium of the alcoholic wine, so that it could be considered a kind of optimum set of parameters for calculating this specific equilibrium. Eventually the changes considered in the parameters values were not able to take them out of this optimum region. On the other hand, the changes of ±5% were performed in the set of parameters as a whole and eventually changes of similar magnitude performed in part of the whole set could have a larger impact on the obtained results. Furthermore, even in the present case the changes in NRTL parameters may have a significant impact on specific results. This occurs in the case of light components concentration in the bottom trays. For instance, the decrease of 1.4% in the alcoholic graduation mentioned above corresponds to a change of approximately 33% in the ethanol concentration in stillage, from 0.0002 to 0.0003.

### 4. Conclusions

The main difference between spirits produced around the world is the concentration of congeners in the beverage. Small changes in the concentration of these congeners are enough for differentiating each spirit. The results presented in this work showed that simple modifications in the distillation column configuration and operational conditions (reflux ratio, second alcohol, degassing stream, spirit flow rate and column trays) are sufficient for producing spirits of different standards. Beverages with moderate alcoholic strength (cachaça, rum, tequila) are easily obtained by simple column systems with a small rectification section. On the other hand, spirits with high alcoholic graduation (whisky, vodka, absinthe and others) require a high reflux ratio and low spirit flow rate, implying higher steam consumption. For these spirits a more complex column system is required. Rectification and stripping sections with a larger number of trays are necessary together with the withdrawal of higher alcohols and second alcohol streams, increasing ethanol losses but allowing for a greater alcoholic graduation (93–96 GL). For spirits with a low volatile contamination, a simple PID controller linked to the degassing system is sufficient to avoid spirit contamination. For spirits with a high alcoholic graduation, the influence of a degassing system on volatile control is not significant because the legislation limits are stricter in this case. Perhaps in this case a control system based on the manipulation of the second alcohol stream is required. These conclusions were made possible because of the ability of commercial simulators, such as Aspen Plus and Aspen Dynamics, to reliably represent the spirit distillation process.
Acknowledgments

The authors thank CAPES, FAPESP (2008/56258-8) and CNPq (304495/2010-7) for the financial support for developing this work.

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