Process simulation applied to studying strategies for spirit distillation from fermented must with high methanol content
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\section*{ABSTRACT}
Methanol is one of the most important congeners present in alcoholic beverages and associated, at high concentrations, with poisoning in humans. Its origin is related to the presence of pectic material in the spirit raw material. Spirits originating from grains and spirits in whose the must fermentation was added vegetables residues with high content of pectin (peel and pomace of fruit) tend to present a higher methanol content. Taking this into account, this work aims to investigate, by process simulation, strategies for continuous spirit distillation from wine (fermented must) with high methanol levels. Aspen Plus process simulator was used for this investigation. A standard solution containing water, ethanol, and 10 congeners represented the fermented must. The spirit production was simulated by one column with 23 stages. The wine was feed into stage 5 (top to bottom) and the spirit was withdrawn from stage 3 with a small second alcohol stream as column distillate. A sensitivity analysis, including the effects of changes in reflux ratio, spirit mass flow, distillate mass flow and the number of stages of the rectifier section, was performed. Their impact on the spirits’ methanol level was investigated aiming to ensure the legislation limits and health of spirit consumers.

\textit{Keywords:} Aspen Plus; Methanol; Distillation; Simulation; Spirit

\section*{INTRODUCTION}
Although methanol has not importance to the spirit flavour, its occurrence has been widely investigated mainly because of it relations with poisoning in humans when ingested in high concentrations. Methanol ingestion can cause blindness or even lead to death [1]. Unlike most of other alcohols present in distilled spirits, the source of methanol is not related to the fermentation process, but to the presence of pectic materials during fermentation [2]. Aiming to improve the sensorial quality of spirits with specific flavours and aromas, pectic wastes, such as fruit pomace and peel, are sometimes added to the must before the fermentation. Most of the methanol present in spirits is then generated by pectin hydrolysis, due to the catalytic action of pectolytic enzymes on the methoxyl group of the poly-carbohydrate molecules [1],[3]. Depending on the raw material for spirits production, the methanol level in the beverage can reach high values, requiring a strict control of its concentration during distillation.

As a consequence of the high methanol toxicity the national regulatory agencies worldwide impose strict limits for its content in spirits. In Brazil, the Ministry of Agriculture, Livestock and Supply (MAPA) set this value to 30 mg of methanol per liter of anhydrous ethanol. In case of the European Union the regulation 1576/89 allows a maximum of 1000 g of methanol per hL of anhydrous alcohol for distilled spirits such as whiskey, marc, rum, wine [4],[5]. Taking into account the high methanol toxicity and the importance of pectic materials for spirit production, this work aims to study some techniques for regulating methanol level in spirits obtained by distillation from fermented musts with high methanol content.

\section*{MATERIALS & METHODS}
A typical industrial plant for distilling Brazilian spirits (cachaça) is represented in Figure 1a. For wine with high methanol level this configuration is inappropriate mainly because of the methanol presence, a light component that concentrates on the top of the column (See methanol column profile in Figure 2a). Because of this fact, the column configuration must be changed, as indicated in Figure 1b.
Figure 1. A typical Brazilian industrial plant for spirits distillation (a) and the simulated configuration (b).

The Aspen Plus software with the RADFRAC package was used for the simulations. This package uses a rigorous calculation method to solve distillation columns, based on the MESH equations [6]. The column has 23 stages (including condenser and reboiler). The wine was fed into stage 5 (top to bottom) with 10000 kg/h at 1 atm. The spirit was withdrawn in stage 3 with a small second alcohol stream as column distillate. No fusel oil was withdrawn. Tray Murphree efficiency was fixed in 0.7. Wine was represented by a standard solution containing water, ethanol and 10 others congeners (Table 1). A normal range of concentrations for methanol was presented and its content was fixed at a value above the upper limit of this range in order to represent a wine with high methanol level. A sensitivity analysis, including changes in reflux ratio, spirit mass flow, distillate mass flow and the number of stage of the rectifier section above of the spirit tray, was performed, so that their impact on the spirit methanol level could be evaluated.

<table>
<thead>
<tr>
<th>Component</th>
<th>Boiling Point (ºC)</th>
<th>Range of concentration (w/w)</th>
<th>Reference</th>
<th>Fixed Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100.0</td>
<td>0.92–0.95</td>
<td>By difference</td>
<td>0.9320712</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78.40</td>
<td>0.05–0.08</td>
<td>[7]</td>
<td>0.06615</td>
</tr>
<tr>
<td>Methanol</td>
<td>64.70</td>
<td>0.0–3.0·10^{-8}</td>
<td>[8]</td>
<td>3.20E-06</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>82.40</td>
<td>1.020·10^{-6}</td>
<td>[9]</td>
<td>1.02E-06</td>
</tr>
<tr>
<td>Propanol</td>
<td>97.10</td>
<td>(2.1–6.8)·10^{-3}</td>
<td>[7]</td>
<td>3.36E-05</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>108.00</td>
<td>(1.3–4.9)·10^{-3}</td>
<td>[7]</td>
<td>2.78E-05</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>132.00</td>
<td>(2.7–18.8)·10^{-3}</td>
<td>[7]</td>
<td>0.001425</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>77.10</td>
<td>(5.5–11.9)·10^{-6}</td>
<td>[7]</td>
<td>7.69E-06</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>20.20</td>
<td>(1.0–8.3)·10^{-3}</td>
<td>[7]</td>
<td>1.58E-05</td>
</tr>
<tr>
<td>Acetone</td>
<td>56.53</td>
<td>-</td>
<td>Estimated</td>
<td>1.50E-05</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>118.10</td>
<td>(3.3–99.3)·10^{-4}</td>
<td>[7]</td>
<td>0.0004351</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-78.00</td>
<td>-</td>
<td>Estimated</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

The equilibrium between the wine components in liquid and vapor phase on each tray can be described by the following equation [10]:

$$\phi_i y_i P = \gamma_i x_i P_{vpi}$$  \hspace{1cm} (1)

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

For this work, NRTL model was chosen for the activity coefficients and the Virial equation, modified by the Hayden and O'Connell model, for the fugacity coefficients.

**RESULTS & DISCUSSION**

The Figure 2b shows that the increase of the second alcohol flow rate increases the spirit methanol content and steam consumption and decreases the spirit alcoholic graduation. Thus, spirit produced from wine with high methanol content requires a low second alcohol flow rate in order to allow a satisfactory alcoholic graduation and steam consumption.

![Figure 2. Methanol profile (120 kg/h second alcohol) (a) and Influence of second alcohol flow rate on methanol level (b).](image)

Figure 2 shows the influence of reflux ratio (a) and spirit mass flow (b) on the methanol content. As can be seen, the increase of both operational conditions increases the spirits methanol content. Spirits produced from wine with high methanol level require low reflux ratios and spirits mass flows. However, low spirits mass flows increase the alcoholic graduation to values even out of the range set by the Brazilian legislation (MAPA, 2005). In this case the spirits must be diluted by the addition of potable water after the distillation process.

Analyzing Figure 2 and Figure 3 is possible to conclude that a combination of low reflux ratios (20), moderated spirits mass flows (almost 1500 kg/h in the present case) and low second alcohol mass flows is sufficient in order to reach the limits imposed by the Brazilian Legislation. However, this technique is only valid for wine with methanol mass fractions below of 3.2x10^{-6}. For higher values of methanol, the best solution is to increase the number of stages in the rectifier column section above the spirit tray. This conclusion is based in the methanol column profile shown in Figure 2a. This figure indicates that increasing the number of trays in the above mentioned section decreases the spirit methanol content.

As can be seen in Figure 4, an increase in the number of trays above spirit tray can reduce considerably the spirit methanol content and reduce the steam consumption. On the other hand, this modification increases the column manufacturing cost. However, taking into account that the steam cost is usually more important than the column manufacturing cost, increasing the number of trays can be rewarding as it will increase the quality of the spirit produced.
CONCLUSION

The Aspen Plus simulator was able to represent the spirits distillation making possible the development of some strategies for producing spirits from wine with high methanol level. For lower methanol wine contamination, below $3.2 \times 10^{-6}$ in mass fraction, the adjustment of the operational conditions was sufficient. Above that limit, the increase of the number of trays in the rectifier section above the spirit tray was more efficient, mainly due to the reduction in the steam consumption.
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REFERENCES