

Heat Transfer Evaluation of Multicomponent Batch Distillation of the Wine of Sugarcane Fermentation

Mario E. T. Alvarez^{a,*}, John H. Bermúdez^a, Elenise B. de Moraes^b, Anderson J. Bonon^a, Maria R. Wolf-Maciel^a

^aSchool of Chemical Engineering, University of Campinas-UNICAMP, Av. Albert Einstein, 500, CEP13083-852, Campinas, SP, Brazil

^bBrazilian Bioethanol Science and Technology Laboratory (CTBE), CP 6170, CEP 13083-970, Campinas-SP, Brazil
mario@feq.unicamp.br

Experimental data and simulations in Aspen Plus[®] for the batch distillation process were obtained from wine of sugar cane fermentation. The experimental data was analyzed in order to verify the effectiveness of the batch distillation process for recovering ethanol, using a packed column. The reflux ratio was maintained equal to two and the temperature of the distillation flask was 180 °C. The distillates and the main components of wine (ethanol, acetaldehyde, acetone, ethyl acetate, n-propanol, n-butanol, 3-methyl-1-butanol, 2-metil-1-propanol, acetic acid, and glycerine) were quantified using gas chromatography analyses. It was found that the highest ethanol concentration was obtained in one hour of distillation and the accumulate ethanol concentration was above 80 % (w/w) when operated at constant reflux. Therefore, it is possible to obtain high yields and concentrations of ethanol in a short period of time.

1. Introduction

In the 1970s, the Brazilian government started a program for the production of ethanol from sugarcane in order to effectively replace gasoline on a large scale. For a time, this program was discontinued, but due to the production instability of the world's largest oil producers and other energy concerns, the search for alternative sources of energy, preferably from renewable sources, has again sparked interest in this subject (Junqueira et al., 2009). The fermentation processes employed in the Brazilian ethanol industry requires low substrate concentration and produce wine of low ethanol content (around 7.0 to 8.5 w/w). When the intention is to use ethanol as a fuel, ethanol concentration must be at least 92.5 to 93.8 w/w. In the batch distillation column, the feed is loaded to the distillation flask at the beginning of the process. It is then heated to its boiling point and the products are withdrawn sequentially from the column's top, according to their boiling point (Demicoli and Stichlmair, 2004). Batch distillation has been used to evaluate the effect of the recycling of foreshots and feints in the grappa distillation (Porto et al. 2010) and in the separation of a complex azeotropic mixture, comparing two methods of separation, showing that the column's hold-ups have influence on the component separation (Watson et al., 1995). In this work, a batch distillation column was used to concentrate ethanol. The distillate fractions containing ethanol, fusel oil and other volatile components were collected and analysed by gas chromatography and the performance of the batch distillation was evaluated. Simultaneously, a simulation using Aspen Plus[®] was performed to evaluate the separation and the heat consumption of the process.

2. Batch Distillation Column

2.1 Details of the batch distillation column

A batch distillation column, model Autodest 800AC of Fischer Technology with a capacity of 80 L was used and conditioned for ethanol distillation. The packed column is filled with Propak 6 mm 316 and equipped with a silvered vacuum mantle. The distillation flask and the packed column have an external heat mantle and the temperature is controlled by a Pt 100. The vapour temperature at the top of the column is also

verified by a Pt 100. In the main condenser, a cryostat was used with a capacity of 360 kcal at 0 °C. The whole system is controlled by Indusoft Web studio™ v6.2 supervisory installed in a PC that allows data acquisition from the batch distillation column.

2.2 Distillation

In order to evaluate the ethanol recovery using batch distillation of wine coming from the fermentation of sugarcane, approximately 50 L of feed mixture, produced in Brazilian alcohol refineries, were used. The distillation was carried out at atmospheric pressure and operating temperatures were adjusted after different experiments. The distillate flask and column temperatures were 180 °C and 80 °C, respectively. The temperature of the cryostat condenser was maintained at 0 °C. When the condensation started at the top of the column, the distillate was withdrawn after 15 min of stabilization of the system and the temperature of the initial vapour was 69°C. During 2 hours, samples were collected every 10 min with a reflux ratio (L/D) equal to two. After distillate fractions were collected, the mixture composition was analysed by gas chromatography.

3. Experimental

3.1 Materials

The reagents, acetaldehyde (≥ 99.0 %, Sigma Aldrich) GC grade, acetone, (≥ 99.9 %, Sigma Aldrich) HPLC grade, ethyl acetate (≥ 99.8 %, Sigma Aldrich) HPLC grade, ethanol (99.9 %, Merck) analytical grade, n-propanol (≥ 99.9 %, Sigma Aldrich) HPLC grade, n-butanol (≥ 99.7 %, Sigma Aldrich) HPLC grade, 2-methyl-1-propanol (≥ 99.0 %, Sigma Aldrich) analytical grade, 3-methyl-1-butanol (≥ 99.0 %, Sigma Aldrich) analytical grade, acetic acid (≥ 99.7 %, Sigma Aldrich) analytical grade, glycerine (≥ 99.5 %, Sigma Aldrich), propionic acid (≥ 99.5 %, Sigma Aldrich) and acetonitrile (≥ 99.9 %, Sigma Aldrich) HPLC grade, were used for analytical methods.

3.2 Analytical Techniques and Procedure

The samples were analyzed in GC-FID (Agilent -6850) equipped with BP-225 – SGE column (50 % - Cyanopropylphenyl Polysiloxane: 25 m x 320 µm x 0.25 µm) using H₂ as carrier gas. GC conditions: Injection volume: 1 µL; Inlet: 250 °C, 5.9 psi with split set at 40:1; Detector: 300 °C, H₂ flow – 35 mL.min⁻¹, Air flow – 300 mL min⁻¹ and make up gas (N₂) flow ≈ 30 mL min⁻¹ (make up + column flow); Oven program: 35 °C hold 6 min; up to 80 °C at 15 °C.min⁻¹, 0 min hold; up to 220 °C at 50 °C min⁻¹, 3,0 min hold; Carrier gas program: 1,0 mL min⁻¹, hold 6 min; up to 3 mL min⁻¹ at 6 mL min⁻², until the end of the run. The quantification was performed with external calibration curves with analytical commercial standards. A calibration curve was made with five different points containing all components to be quantified. Propionic acid and acetonitrile were used as internal standards for quantified ethanol and higher alcohols, respectively. All analyses were carried out in duplicate.

4. Simulations

Aspen Plus® was used to simulate the batch distillation process. Simulations in this work were made considering a packed column with the same characteristics of the experimental distillation column. The feed temperature was maintained at 180 °C. The simulation was carried out at atmospheric pressure and the feed charged was assumed to be 50 L. The setup block was considered to be 10 min of feed time in the initial charge. The stop specification was defined as 2 h of distillation. The reflux ratio was equal to two. The packing specification for the column was: section diameter 0.61 mm, HETP 69.47 mm (ASTM D2892, 2005), Voidage 0.96, Specific surface 372 ft²/ft³ and the thermodynamic model used was NRTL. Simulations were made and the required heat was determined in order to carry out the batch distillation. The heat duty was expressed in function of time.

5. Results and discussion

The wine of sugar cane fermentation coming to Brazilian alcohol refineries, used in this work, showed the following composition.

Table 1: Composition of wine of sugar cane fermentation

Component	Composition	Units
acetaldehyde	6.37	(mg/L)
acetone	163.85	(mg/L)
ethyl acetate	10.59	(mg/L)

Component	Composition	Units
ethanol	6.62	(w/w %)
n-propanol	19.14	(mg/L)
n-butanol	3.25	(mg/L)
2-methyl-1-propanol	33.97	(mg/L)
3-methyl-1-butanol	90.15	(mg/L)
acetic acid	235.90	(mg/L)
glycerine	699.91	(mg/L)

The sample was analysed using Gas Chromatography and the results show that ethanol is the main component produced in the fermentation, however, other substances are also obtained. Glycerine is the component with the highest quantity. Nevertheless, due its high boiling point, this component is concentrated in the same distillation flask.

Experimental data results for batch distillation are presented in Figure 1 up to Figure 9. It was observed that the ethanol composition was between 90 to 70 % (w/w) in the first 80 min of distillation. After this time, there was a sharp decline in ethanol composition, reaching values close to 65 % (w/w). It was also observed that during the distillation operation, the other components were still present in the distillate. The 3-methyl-1-butanol in Figure 2 is represented as a percentage because this component has the greatest concentration in the distillate.

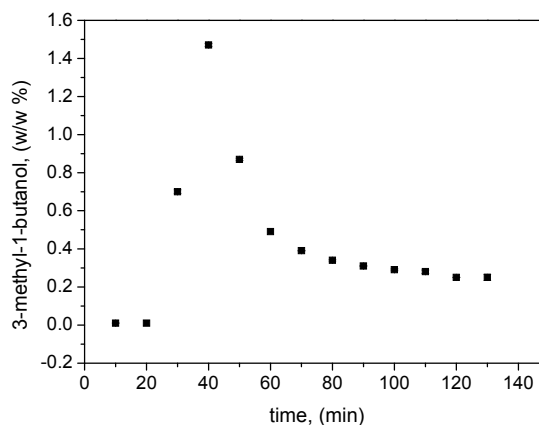
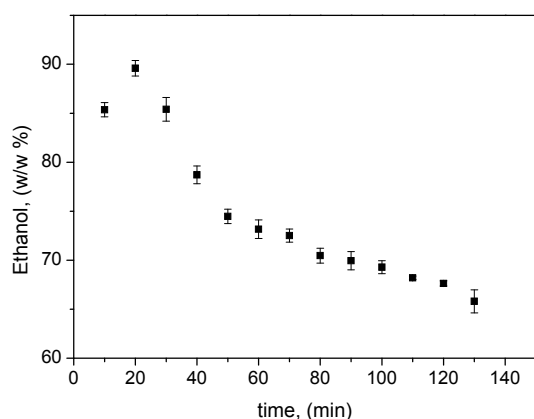


Figure 1: Variation of the ethanol composition in the Distillate vs time

Figure 2: Variation of the 3-methyl-1-butanol composition in the Distillate vs time

In Figure 3, the presence of acetaldehyde is observed in all distillate fractions collected. Although acetaldehyde has high volatility, this component is not completely separated in the beginning of the distillation process. The highest concentration of acetone (Figure 4) is obtained during the first minutes, after that, the concentration decreases to 6 ppm. This demonstrates that acetone is not present in large quantities in the distillate when compared to other components. All components were removed in the first minutes of distillation, so it can be observed in Figures 3 - 4 and 6 - 9 that, after 40 min, their compositions are lower than 40 ppm. On the other hand, observing Figure 5, it can be verified that 2-methyl-1-propanol remains at 100 ppm; this explains that 2-methyl-1-propanol and 3-methyl-1-propanol (Figure 2) are alcohols tightly bound in the distillation of ethanol.

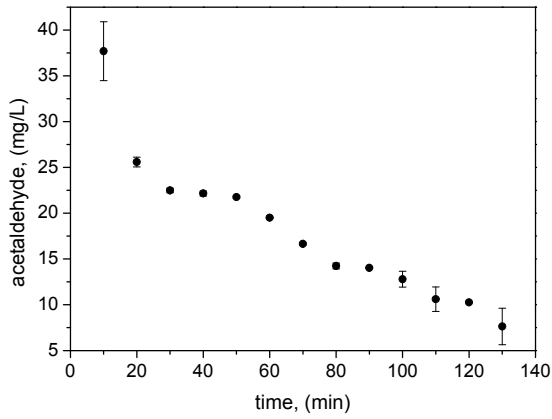


Figure 3: Variation of the acetaldehyde composition in the Distillate vs time

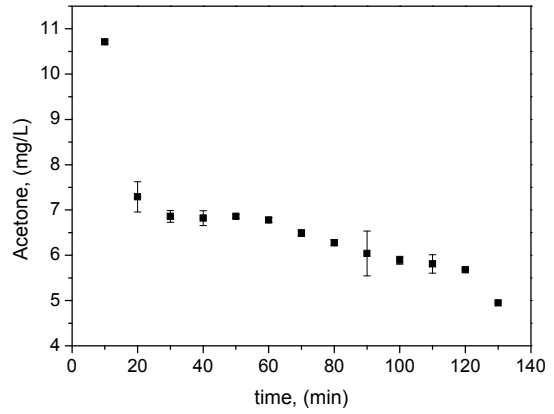


Figure 4: Variation of the acetone composition in the Distillate vs time

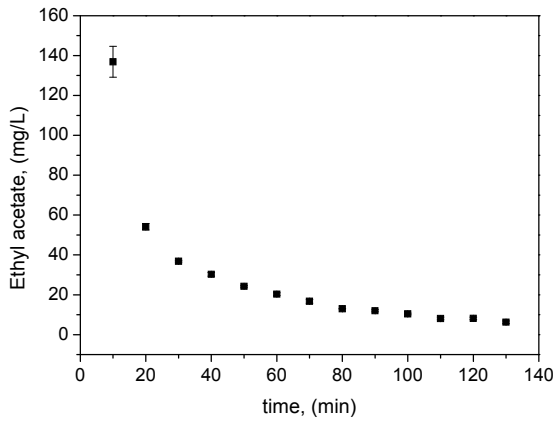


Figure 5: Variation of ethyl acetate composition in the Distillate vs time

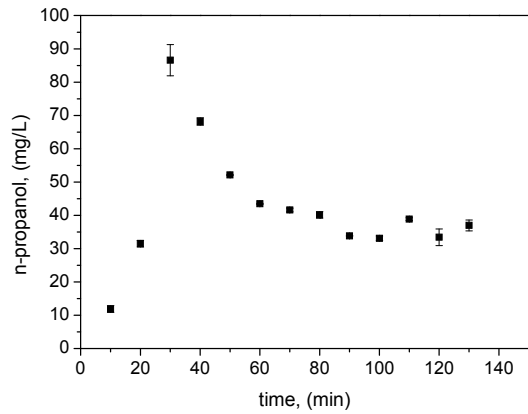


Figure 6: Variation of the n-propanol composition in the Distillate vs time

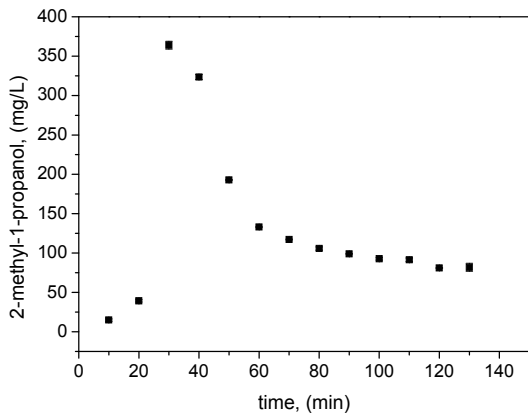


Figure 7: Variation of the 2-methyl-1-propanol composition in the Distillate vs time

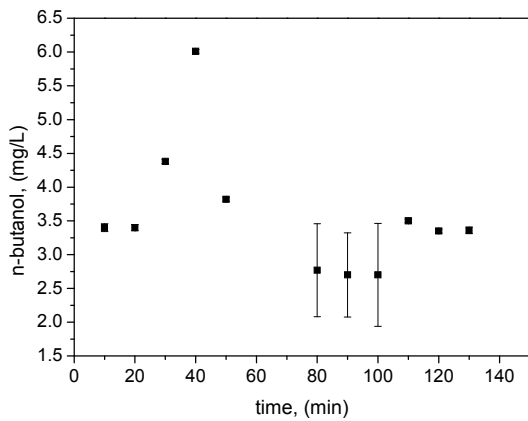


Figure 8: Variation of the n-butanol composition in the Distillate vs time

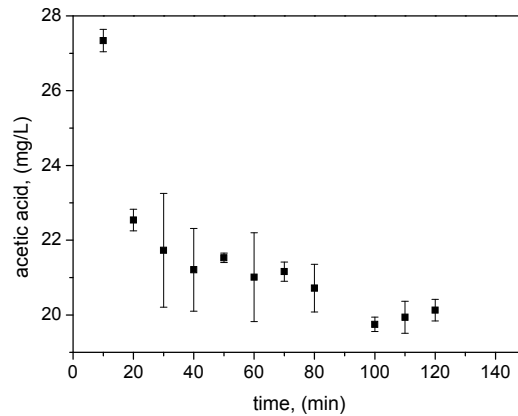


Figure 9: Variation of the acetic acid composition in the Distillate vs time

The simulation in Aspen Plus® was performed considering all variables and specifications of the experimental column.

Figures 10 and 11 show the results of the heat duty versus time for the distillation flask and condenser, respectively. It is observed that, at the beginning of the distillation, the heat duty reaches a maximum level due to the necessary heat required to raise the feed temperature to the boiling point of the components, while the condenser shows a higher heat duty necessary for condensing the steam at the top of the column. The heat duty decreases over time until it reaches a drop of 30 % after 2 h. This is due to the separation and the removal in the distillate stream of the volatile components present in the initial charge.

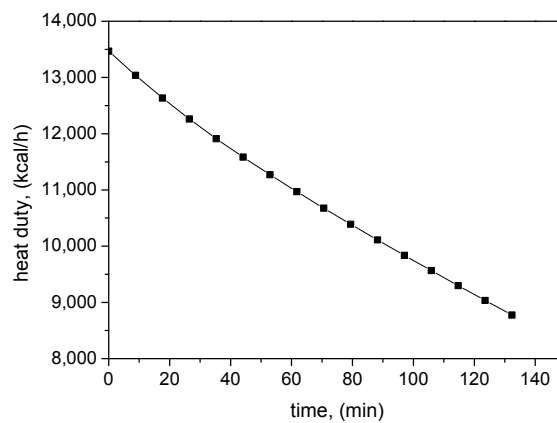


Figure 10: Heat duty in Distillation Flask vs time

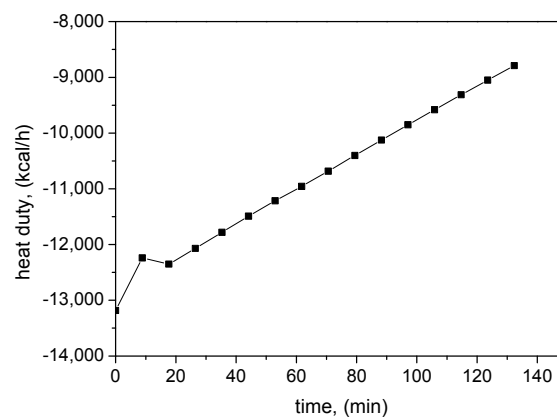


Figure 11: Heat duty in Condenser vs time

6. Conclusions

Experimental data of wine from sugar cane distillation was obtained and evaluated for the separation of multicomponent mixture through a batch distillation process using a packed column. A method was developed to quantify the multicomponent mixture through gas chromatography analyses. The samples were analyzed in duplicate and they showed good accuracy. It is possible to recover ethanol above 65 % (w/w) in two hours. Also, it was verified that the other components were separated in each distillate fraction.

It was observed that the heat duty required to heat the feed can reach 13,500 kcal/h during the distillation process. The heat duty decreases down to 70 % of the initial value, reaching values around 9,000 kcal/h. The effect on the heat duty for the condenser is similar.

Acknowledgements

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References

- American Society for Testing Material, ASTM D 2892, 2005, Standard test method for distillation of crude petroleum (15-theoretical plate column), West Conshohocken, (Pennsylvania): ASTM International, 32p.
- Demicoli D., Stichlmair J., 2004, Separation of ternary mixtures in a batch distillation column with side withdrawal, *Computers Chem. Engng.* 28, 643-650.
- Junqueira T.L., Dias M.O.S., Maciel M.R.W., Filho R.M., Rossell C.E.V., Atala D.I.P. 2009. Simulation and optimization of the continuous vacuum extractive fermentation for bioethanol production and evaluation of the influence on distillation process, *Computer Aided Chem. Engng.* 26, 827-832. DOI: 10.1016/S1570-7946(09)70138-5
- Porto C., Natolino A., Corti D. 2010. Batch distillation of grappa: effect of the recycling operation, *Int. J. Food Sci. Tech.* 45, 271-277. DOI: 10.1111/j.1365-2621.2009.02131.x
- Watson S., Joulia X., Macchietto S., Le Lann J.M., Vayrette G., Letourneau J.J. 1995. Azeotropic batch distillation new problems and some solutions, *Computers Chem. Engng.* 19, S589-596.