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Article

Non-Conventional Cuts in Batch Distillation to Brazilian Spirits (*cachaça*) Production: A Computational Simulation Approach

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Abstract: In this work, an algorithm was developed to determine different possibilities of distillation cuts to support productivity and improve the final quality of *cachaça*, a Brazilian spirit beverage. The distillation process was simulated using the Aspen Plus® software, considering a wide range of fermented musts compositions available in the literature obtained by fermentation with different yeast strains. Twenty-four simulations were carried out considering eight compounds as follows: water and ethanol (major compounds); acetic acid, acetaldehyde, ethyl acetate, 1-propanol, isobutanol, and isoamyl alcohol (minor compounds). The calculations considered a long-time process, i.e., until almost all the ethanol in the fermented must was distilled. The algorithm enabled the identification of countless distilling cuts, resulting in products with different alcoholic grades and process yields. One fermented must became viable to produce *cachaça* after the suggested non-traditional method of cuts proposed in this work. Furthermore, the non-traditional distilling cut provided a productivity gain of more than 50%. Finally, the ratio of acetaldehyde and ethanol concentration was the key parameter to determine whether the fermented musts could provide products meeting *cachaça*'s legislation.

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1. Introduction

Spirits correspond to alcoholic beverages produced by fermentation of several raw materials, followed by distillation, and contain at least 15% v/v ethanol [1–3]. The quality and specific characteristics of a spirit beverage highly depend on the nature and concentration of congeners compounds, such as alcohols, carboxylic acids, esters, and aldehydes. The diversity and concentration of these compounds are mainly an outcome of the raw material, fermentation, and distillation process [4].

Depending on the raw material used in the fermentation and the geographical indication, spirits can have different names. For instance, whisky is produced by the distillation of fermented grain mash [5]; vodka is produced from grain or potato fermented must [6]; rum is produced by the distillation of sugar cane and molasses [7]; tequila is obtained by the distillation of fermented juice from the agave plant [8]; and *cachaça* is produced by the distillation of fermented sugar cane juice [1]. The concentration of congeners (minor compounds) presented at a low concentration in the fermented must, and, thus, in the beverage, are responsible for characterizing each type of spirit [1,9], evidencing the importance of fermentation in spirit quality [4]. The composition of volatile compounds is also influenced by the apparatus and the distillation method [4]. The behavior of volatile compounds is different during distillation in pot stills and rectification columns. For instance, higher alcohols, responsible for a strong influence on the perceived flavor of distillate beverages, are recovered in larger quantities in the distillate in continuous distillation than in a simple batch process [10].

Cachaça is an exclusive designation of sugar cane spirit beverage typical of Brazil, with an alcohol content of 38 to 48% *v*/*v*, at 20 °C [11,12]. According to the Brazilian Institute of Geography and Statistics (IBGE), in the last census, performed in 2017, the Brazilian production of *cachaça* was approximately 83.4 million liters by 11,028 producers [13]. Almost 80% of this production is related to family agricultural (artisanal) production. In 2021, 7.3 million liters of *cachaça* were exported to 70 countries, providing an income of US$13.2 million [14]. Besides its economic importance, *cachaça* is a part of the Brazilian heritage, being the Brazilian iconic spirit and ingredient for the world-famous drink caipirinha [15–17].

Cachaça production can be summarized as follows: raw material preparation, sugar cane juice extraction, fermentation, and distillation to ethanol concentration [18]. Before commercialization, the product is stored in an inert vessel to improve sensory qualities and may be aged in wooden barrels [18]. Fermentation strongly influences the final product quality, as it is the step responsible for forming secondary products, such as higher alcohols, organic acids, carboxylic compounds, and esters, also responsible for the beverage's sensorial characteristics [19,20]. Several works have demonstrated the influence of fermentation on the quality and geographical indication of *cachaça* [15,16,21,22].

The fermentation product of sugar cane juice, known as fermented must (wine, in the Brazilian industrial jargon), goes to the distillation process, the unity operation responsible for concentrating ethanol [19]. Distillation is also responsible for lowering propanol and acetaldehyde contents and reducing methanol to minimum levels, due to its high potential to cause intoxication [23]. *Cachaça* production in a batch process, and likewise for other spirits, accounts for three distilling cuts, known as head, heart, and tail [24]. The first 1 to 2% of effective boiler volume, known as the head, presents higher amounts of highly volatile minor compounds (acetaldehydes, methanol, and ethyl acetate), usually discarded [15,19]. The heart is the essential cut, presenting high ethanol concentration and corresponding to the final product. The tail presents a high concentration of water-soluble volatiles (mostly acetic acid and furfural) [15,19]. The final product (heart) must follow a restricted chemical composition, considering Brazilian legislation regarding safety and sensorial qualities [11]. However, according to Bortoletto and Alcarde [25], more than half of *cachaças* produced and commercialized in Brazilian local markets are not in compliance with the identity and quality standards established by Brazilian legislation.

Currently, the separation of fractions of distillate from sugar cane fermented must in artisanal pot stills is done in a prominently empirical and standardized manner, based on ideal fermented must composition, without considering differences arising from the fermentation of different yeast strains. Oliveira et al. [20] showed that different yeast strains produce fermented musts with different compositions of minor compounds. Even though several works have evidenced the importance of minor compounds in spirit quality, regarding the influence of fermentation processes and yeast strains on fermented must quality, the study of the impact of distilling cuts on minor compounds is still scarce.

Process simulation is a convenient tool that has already been widely applied to understand and optimize spirit distillation and predict its volatile aroma. Some works demonstrated the effect of distillation parameters on volatile aroma compounds and spirit quality [1,24,26–32]. However, none of the works mentioned focused on studying distilling cuts to improve *cachaça* quality and yield.

This work simulates the *cachaça* distilling cuts to support productivity and improve final product quality. The distillation process was simulated with the Aspen Plus® software, considering the composition of real fermented must available in the literature obtained by fermentation with different yeast strains and a long distillation time until almost all the ethanol in the fermented must was distilled. Then, an algorithm was developed to establish several possibilities of distilling cuts that result in *cachaça*, according to Brazilian legislation. To the best of the author's knowledge, this work is a pioneer in analyzing how the distilling cut may be used to overcome bad fermented musts, that at a first reckoning could not be used to produce spirits within the legislation.

This work is organized as follows. Section 2 presents the simulation details, these being the VLE calculation and simulation approach, the description of a common commercial alembic, the initial concentration of fermented musts available from the literature and the algorithm proposed in this work. Section 3 describes the results in terms of a comparison between experimental and simulated results, an analysis of "cachaça" distilling cuts, an evaluation of the most important minor compounds influencing distilling cut, a description of new distilling cut possibilities and their yield improvements. In Section 4, the conclusions and perspectives on future works are presented.

2. Methods

2.1. Simulation of Pot Still Distillation

Pot still simulations were conducted with the Aspen Plus® Simulator (AspenTech, Bedford, MA, USA), version 12.0, using the BatchSep package, which performs rigorous dynamic simulations for batch distillation columns [33]. The simulation assumed equilibrium stages, constant liquid holdup, no vapor holdup, and non-modeled hydraulics. The simulated equipment consisted of a pot still and a total condenser, with dimensions based on those found in commercial equipment [34]: elliptical shape, vertical orientation, 0.33 m diameter, 0.35 m height, and 40 L volume (Figure 1). Thus, the system presented only one equilibrium stage with ideal vaporization efficiency. The initial operation conditions were 30 kg of initial fermented must charge, reflux ratio 0.8, 1 atm inside the pot, 10% pressure drop between the pot still and the condenser, and 2.5 kW effective coil power. Calculations were performed until ethanol concentration in the distillate reached 31% (*w/w*), approaching from above, extrapolating the lower limit of 38% (*v/v*) provided for in Brazilian legislation.

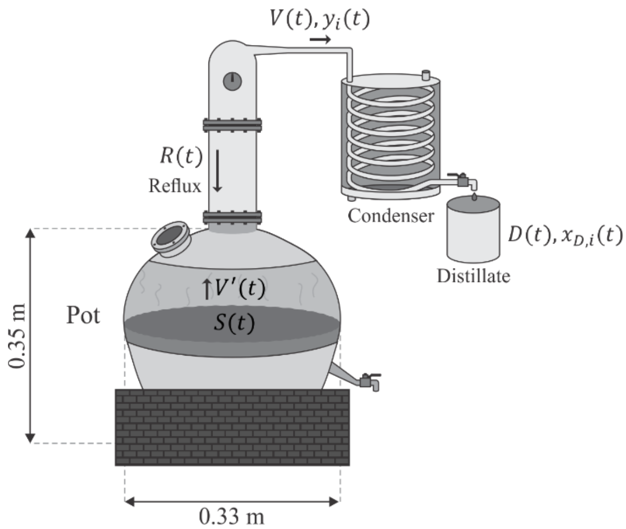

Figure 1. Scheme of pot still geometry used for simulations.

2.2. Vapor–Liquid Equilibrium

The vapor–liquid equilibrium was calculated considering the gamma–phi approach, allowing the description of non-idealities of both phases [35]. The literature demonstrates that the vapor phase may be described as ideal due to the low pressure and concentration of gas [26,36], except for carboxylic acids, which can form dimers, due to strong hydrogen bonds [4]. Thus, the virial equation of state, coupled with the Hayden O'Connell model, was used to describe the vapor phase. The liquid phase was described by NRTL (Non-Random Two Liquids), which is the best model to describe hydroalcoholic solutions [1,3,37]. From this point forward, this thermodynamic approach is referred to as the so-called NRTL-HOC. The NRTL parameters are available in the Supplementary material.

2.3. Validation

Experimental data from Scanavini [38] were used as a reference to check the simulation reliability. The simulation module was set up as reported previously. The simulated equipment consisted of a pot still and a total condenser, with dimensions described by Scanavini [38], having an elliptical shape, vertical orientation, 0.31 m diameter, and 8 L volume. The system presented only one equilibrium stage with ideal vaporization efficiency. The initial operational conditions were as follows: 2 kg of initial fermented must load, null reflux, 1 atm inside the pot, 10% pressure drop between the pot still and the condenser, with the mole boil-up rate of 0.011 mol/s. Calculations were performed until the distillate receiver's total mass holdup reached 1916 kg, approaching from below. The experimental and simulated distillate compositions of eight compounds (ethanol, acetaldehyde, methanol, isobutanol, 1-propanol, isoamyl alcohol, acetic acid, and ethyl acetate) were compared. The vapor–liquid equilibria were described by NRTL-HOC, as described in the previous section.

2.4. Fermented Must Composition

Simulations were performed with a fermented must composed of eight compounds. Water and ethanol were the major compounds. Acetic acid, acetaldehyde (ethanal), ethyl acetate, 1-propanol, isobutanol (2-methyl-1-propanol), and isoamyl alcohol (3-methyl-1-butanol) were the minor compounds. These minor compounds are significantly present in fermented musts and are restricted by Brazilian legislation [11,20]. Twenty-four simulations were carried out with the fermented must compositions available in the literature (Table 1) [22]. The fermented must compositions were obtained by fermentation using yeast strains belonging to the species *Saccharomyces cerevisiae*, *Pichia subpelliculosa*, and *Kloeckera javanica*, isolated from an artisanal producer in the state of Minas Gerais, an important producing region in Brazil. The exceptions were two fermented musts obtained by yeasts from an industrial producer and Sc24 (c5), obtained by yeasts from an alcohol distillery [22].

Table 1. Mass composition (%) of fermented musts used as the initial charge for pot still simulation [22].

	Ethanol	Acetic Acid	Acetaldehyde	Ethyl Acetate	n-Propanol	Isobutanol	Isoamyl Alcohol	Water
c1	7.25	0.0273	1.35×10^{-3}	6.40×10^{-4}	2.13×10^{-3}	1.35×10^{-3}	9.74×10^{-3}	92.71
c2	7.07	0.0296	1.80×10^{-3}	9.37×10^{-4}	3.41×10^{-3}	1.80×10^{-3}	12.88×10^{-3}	92.87
c3	6.99	0.0436	1.58×10^{-3}	7.87×10^{-4}	3.37×10^{-3}	2.78×10^{-3}	14.29×10^{-3}	92.95
c4	6.99	0.0492	1.63×10^{-3}	9.09×10^{-4}	2.56×10^{-3}	1.82×10^{-3}	10.96×10^{-3}	92.95
c5	6.90	0.0460	0.95×10^{-3}	6.73×10^{-4}	2.93×10^{-3}	1.77×10^{-3}	11.38×10^{-3}	93.04
c6	6.90	0.0534	1.19×10^{-3}	7.45×10^{-4}	2.94×10^{-3}	1.82×10^{-3}	16.00×10^{-3}	93.03
c7	6.81	0.0409	1.26×10^{-3}	8.46×10^{-4}	2.53×10^{-3}	2.54×10^{-3}	14.53×10^{-3}	93.13
c8	6.81	0.0848	1.64×10^{-3}	9.64×10^{-4}	3.41×10^{-3}	1.69×10^{-3}	12.85×10^{-3}	93.09
c9	6.81	0.0401	1.32×10^{-3}	8.15×10^{-4}	2.97×10^{-3}	1.81×10^{-3}	16.42×10^{-3}	93.13
c10	6.72	0.0636	1.23×10^{-3}	1.08×10^{-3}	3.24×10^{-3}	2.29×10^{-3}	14.43×10^{-3}	93.19
c11	6.63	0.0887	1.39×10^{-3}	5.85×10^{-4}	4.25×10^{-3}	1.46×10^{-3}	10.79×10^{-3}	93.26
c12	6.54	0.0590	1.03×10^{-3}	7.90×10^{-4}	3.40×10^{-3}	2.10×10^{-3}	13.26×10^{-3}	93.38
c13	6.44	0.0537	1.22×10^{-3}	7.12×10^{-4}	2.71×10^{-3}	1.75×10^{-3}	10.69×10^{-3}	93.49
c14	6.44	0.0207	1.38×10^{-3}	5.17×10^{-4}	2.92×10^{-3}	1.37×10^{-3}	9.818×10^{-3}	93.52
c15	6.44	0.0308	1.66×10^{-3}	6.15×10^{-4}	2.30×10^{-3}	1.78×10^{-3}	9.877×10^{-3}	93.51
c16	6.36	0.0216	1.94×10^{-3}	6.87×10^{-4}	2.93×10^{-3}	1.93×10^{-3}	7.954×10^{-3}	93.61
c17	6.35	0.0502	2.16×10^{-3}	6.06×10^{-4}	3.95×10^{-3}	1.50×10^{-3}	12.18×10^{-3}	93.58
c18	6.27	0.0390	2.03×10^{-3}	7.87×10^{-4}	2.58×10^{-3}	1.66×10^{-3}	8.35×10^{-3}	93.68
c19	6.09	0.0320	1.28×10^{-3}	6.52×10^{-4}	2.46×10^{-3}	1.40×10^{-3}	9.49×10^{-3}	93.86
c20	6.00	0.0248	2.77×10^{-3}	5.31×10^{-4}	2.68×10^{-3}	1.31×10^{-3}	9.03×10^{-3}	93.96
c21	5.74	0.0480	2.53×10^{-3}	5.81×10^{-4}	3.10×10^{-3}	1.94×10^{-3}	9.49×10^{-3}	94.20
c22	5.48	0.0281	2.94×10^{-3}	6.82×10^{-4}	2.31×10^{-3}	1.20×10^{-3}	9.08×10^{-3}	94.48
c23	5.39	0.0237	1.63×10^{-3}	5.01×10^{-4}	4.91×10^{-3}	2.07×10^{-3}	13.63×10^{-3}	94.56
c24	5.13	0.0037	2.05×10^{-3}	7.28×10^{-4}	1.57×10^{-3}	3.39×10^{-3}	9.75×10^{-3}	94.85

2.5. Algorithm to Determine Distilling Cuts

The mass fraction of distillate for each compound $w_{D,i}(t)$ and the total mass of distillate were calculated by BatchSep for every twenty seconds of each batch (dt = 20 s). The molar fractions obtained by Aspen Plus were organized and used as input for the algorithm (Figure 2), implemented in Fortran to determine the possibilities of distilling cuts resulting in a product obeying the legislation. *Cachaça* and its composition were mathematically defined according to Equations (1) and (2), respectively.

$$C(t_1, t_2) \equiv D(t_2) - D(t_1) \quad (1)$$

$$w_i(t_1, t_2) \times C(t_1, t_2) \equiv w_{D,i}(t_2) \times D(t_2) - w_{D,i}(t_1) \times D(t_1) \quad (2)$$

C is the amount of *cachaça* (kg), D is the total amount of distillate generated until the selected time, and t_1 and t_2 correspond to the selected time for the first and second cuts, respectively. The subscript D is related to the distillate, and i to the compound. The *cachaça* composition ($w_{D,i}$) was tested for every pair t_1 and t_2, as described in the algorithm (Figure 2): if the composition obeyed the Brazilian legislation (Table 2), the data set was stored in a file for further analysis.

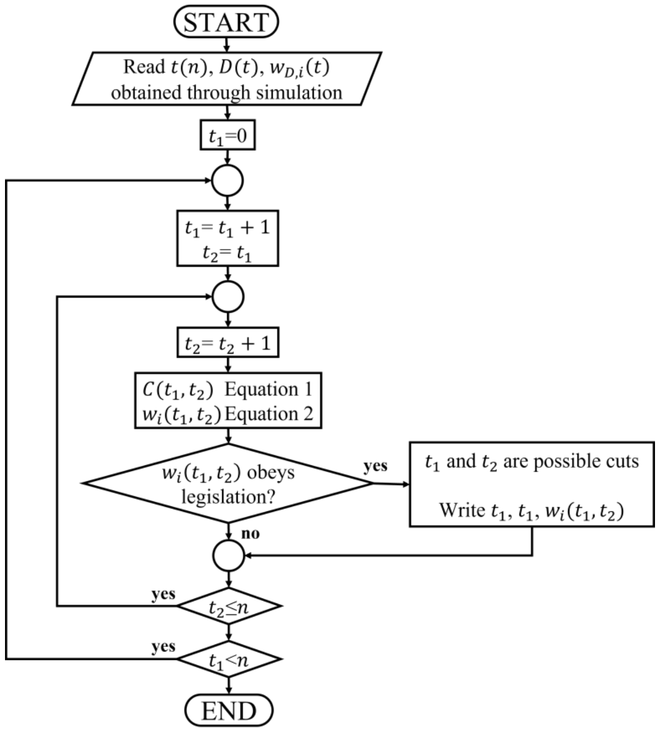

Figure 2. Algorithm for determining the distilling cuts of *cachaça*.

Table 2. Limits for the minor compounds of *cachaça* imposed by Brazilian Legislation [11].

Component	Unit	Limits	
		Lower	Upper
Ethanol	% (v/v) at 20 °C	38	48
Volatile acidity (expressed in acetic acid)	mg/100 mL AA [a]	-	150
Total esters (expressed in ethyl acetate)	mg/100 mL AA [a]	-	200
Total aldehydes (in acetaldehyde)	mg/100 mL AA [a]	-	30
Higher alcohols [b]	mg/100 mL AA [a]	-	360
Methanol	mg/100 mL AA [a]		20

[a] AA anhydrous alcohol; [b] higher alcohols = 1-propanol + isobutanol + isoamyl alcohol.

3. Results

3.1. Validation

In this work, batch distillation simulations were performed to evaluate possible distilling cuts in cachaça production from fermented musts obtained through fermentation using several yeast strains. A simulation was performed using data available in the scientific literature. These simulations were performed under the same operational conditions as Scanavini [38] reported. The relative deviation between experimental and simulated data decreased through the process, presenting good agreement (Figure 3). This difference may be explained by small fluctuations in process parameters during the beginning of the experimental batch process [38]. The simulation of batch distillation calculated, for each time, the molar fraction of component *i* that was being vaporized. The amount vaporized was then defined by multiplying this mole fraction by the amount of liquid inside the pot still. In this way, small differences in the vaporized mole fraction were amplified when there was more liquid in the pot still, such as at the beginning of the process. For the same reason, the experimental data from Scanavini [38] showed greater oscillations at the beginning of distillation.

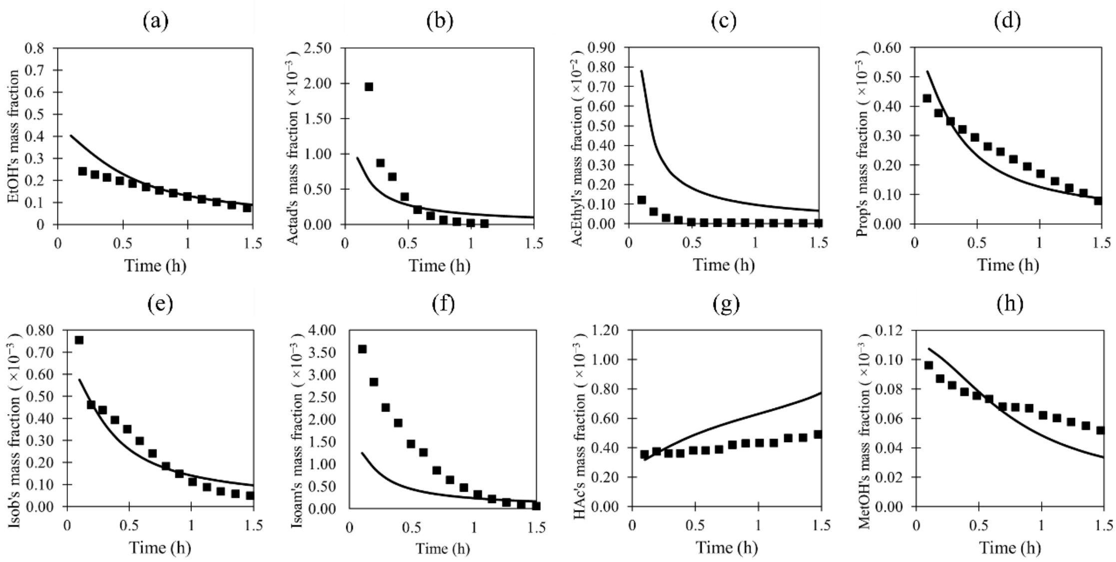

Figure 3. Experimental (■) and simulated (line) concentration profiles for the eight studied compounds: (**a**) ethanol, (**b**) acetaldehyde, (**c**) ethyl acetate, (**d**) 1-propanol, (**e**) isobutanol, (**f**) isoamyl alcohol, (**g**) acetic acid, (**h**) methanol. Simulations were performed using the NRTL-HOC model.

Figure 4 shows the average absolute deviation (AAD) between experimental and simulated data. The AAD for ethanol was 0.03, with values in the same order of magnitude as those found in the literature for batch distillation. The other studied compounds presented absolute relative deviations lower than 0.002, with a good agreement of the behavior profile. The only exception was the behavior profile of acetic acid composition. Despite the differences, experimental and simulated acetic acid concentrations showed an increasing trend. Other studies also observed higher absolute deviation for acetic acids, due to the challenges of quantifying this component in hydroalcoholic solutions [1,19].

3.2. Simulation of Traditional Distilling Cuts

The distillation process was simulated considering the traditional distilling cuts widely used by Brazilian producers: the head ranged from 1.94 to 2.00% of the initial fermented must volume and the heart was defined when the product achieved an average alcohol concentration of 38% (v/v) [15]. The process design is specified in Table 3, which includes the input nominal operating conditions. Of 24 fermented musts, 9 had a distillate composition that did not obey the limits for congeners stipulated by Brazilian legislation (Table 4).

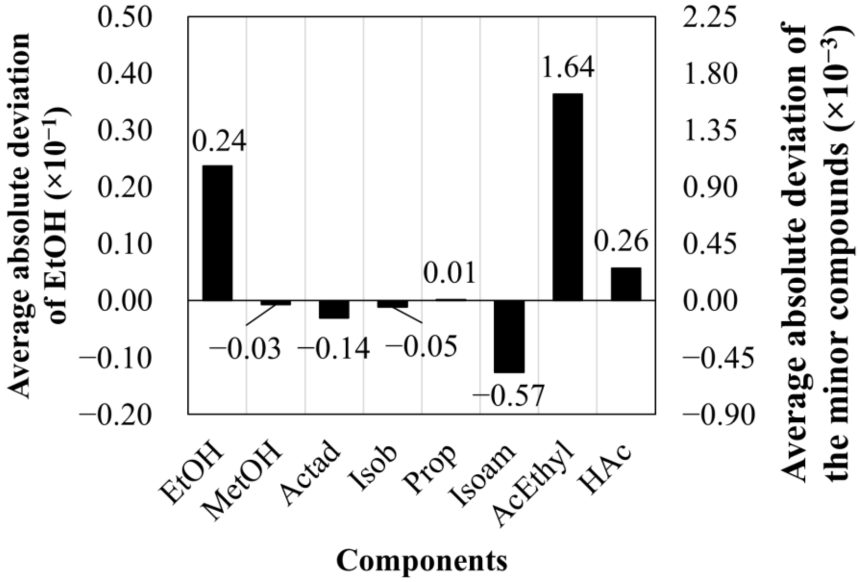

Figure 4. The average absolute deviation between simulated and experimental data for the eight studied compounds (% *w/w*). EtOH = ethanol, MetOH = methanol, Actad = acetaldehyde, Isob = isobutanol, Prop = n-propanol, Isoam = Isoamyl alcohol, AcEthyl = Ethyl acetate, HAc = Acetic acid.

Table 3. Input parameters, pot geometry and initial operational conditions for the simulation of fermented must distillation.

Input Parameters	Value
Process configuration	Pot + Overhead condenser
Number of equilibrium stages	1
Vapor–liquid equilibrium model	NRTL-HOC
Condenser type	Total
Vaporization efficiency	Ideal
Pot Geometry	
Orientation	Vertical
Top geometry	Elliptical
Bottom geometry	Elliptical
Diameter	0.33 m
Height	0.35 m
Volume	40 L
Initial Operation Conditions	
Total initial charge	30 kg
Fermented must composition	Variable
Reflux ratio	0.8
Pot pressure	1 atm
Pressure drop (between the pot still and the condenser)	10%
Effective coil power	2.5 kW
Stop condition	31 wt% of EtOH in distillate

The compositions c15, c16, c17, c18, c20, c21, c22 and c23 had an acetaldehyde concentration higher than allowed; and c23 showed an excess of higher alcohols. Furthermore, c24 did not provide a minimum of 38% of ethanol (v/v) when submitted to the traditional cut and c24 was the only fermented must obtained by *Kloeckera javanica*, indicating that this isolated strain should not be used to produce cachaça. Strategies can be implemented to modify the distillation process, enabling better use of fermented musts with problematic fermentations [18,19,39]. The yield, defined as the ratio in mass of distillate and fermented musts, ranged from 5.5 to 11.4% by applying traditional cuts. Therefore, an analysis of the distilling cuts was expected to guide quantitative improvement and diversification of cachaça quality.

Table 4. The concentration of minor compounds obtained from traditional cuts for each fermented must composition (mg/mL of Anhydrous Alcohol).

	Acetaldehyde	Acetic Acid	Ethyl Acetate	Higher Alcohols
c1	18.65	26.68	3.40	194.87
c2	26.40	29.05	5.33	278.23
c3	23.96	42.67	4.61	322.33
c4	24.68	48.03	5.31	241.62
c5	14.81	44.59	4.08	259.27
c6	18.58	51.88	4.52	337.22
c7	20.39	39.86	5.35	325.32
c8	26.48	82.42	6.04	295.94
c9	21.34	39.07	5.11	353.15
c10	20.61	61.68	7.05	339.26
c11	23.83	85.97	4.05	285.21
c12	18.37	57.10	5.56	334.96
c13	22.67	51.99	5.21	278.98
c14	25.51	19.95	3.82	259.28
c15	**30.65**	29.85	4.50	256.96
c16	**37.58**	20.75	5.42	239.20
c17	**41.74**	48.31	4.83	333.68
c18	**40.89**	37.58	6.58	243.66
c19	27.91	30.65	6.16	276.15
c20	**63.25**	23.63	5.48	276.92
c21	**66.30**	45.60	7.85	338.69
c22	**89.48**	26.61	12.98	329.30
c23	**52.13**	22.36	11.70	**552.27**
c24 *	**-**	**-**	**-**	**-**

Compositions in bold: the traditional cut products do not meet the *cachaça*'s legislation for minor compounds; * the fermented must do not provide a minimum of 38% of ethanol (v/v) by the traditional cut.

3.3. Evaluation of Nonconventional Distilling Cuts

Aiming to improve process yield, the algorithm previously presented was implemented to evaluate the possible distilling cuts. Firstly, data were evaluated regarding yield improvement (Table 5). The maximum process yield ranged from 15.0 to 8.6% in mass. This represented a yield gain of up to 3.7% in relation to traditional cuts. The algorithm provided an alternative cut for c15 with minor compounds within the legislative limits and a yield of 8.6%. From another perspective, the productivity gains, i.e., mass quantity of cachaça obtained with nonconventional cuts in relation to that obtained by traditional cuts, were estimated. Compositions c13 and c19, as mentioned, showed a productivity gain of more than 50% if non-traditional cuts were applied.

Table 5. The maximum yield achieved by nonconventional distilling cuts and its respective yield and productivity gain in relation to the traditional distilling cut.

	Yield [a]	Max. Yield [b]	Yield Gain [c]	Productivity Gain [d]
c1	11.4	15.0	3.6	31.9
c2	10.6	14.0	3.4	31.6
c3	10.2	13.7	3.6	35.3
c4	10.2	13.7	3.6	35.3
c5	9.7	13.3	3.6	36.9
c6	9.7	13.3	3.6	37.4
c7	9.3	12.9	3.6	38.5
c8	9.3	12.7	3.4	36.7
c9	9.3	12.1	2.8	30.5

Table 5. *Cont.*

	Yield [a]	Max. Yield [b]	Yield Gain [c]	Productivity Gain [d]
c10	8.9	12.4	3.6	40.5
c11	8.4	12.0	3.6	42.6
c12	7.9	11.5	3.7	46.8
c13	7.4	11.0	3.7	**50.0**
c14	7.4	11.0	3.7	40.0
c15	**NA**	**8.6**	**NA**	**NA**
c19	5.5	8.6	3.1	56.3

[a] Yield = (100 × kg distillate/kg fermented must). [b] after all studied distilling cuts; [c] in relation to the traditional cut; [d] mass quantity of *cachaça* obtained with nonconventional cuts in relation to that obtained by traditional cuts; **Compositions in bold:** the traditional cut products did not meet the *cachaça*'s legislation for minor compounds; NA = not available, as there was no traditional cut.

Following on from this, the influence of each compound on the distilling cuts was analyzed. Figure 5 presents the characteristic representations developed in this work, for possible distilling cuts based on compound concentration. All the shaded regions represent distilling cuts that provided *cachaças* meeting the Brazilian legislation. The diagonal lines represent the yields. The darker the regions, the higher the ethanol content of the product.

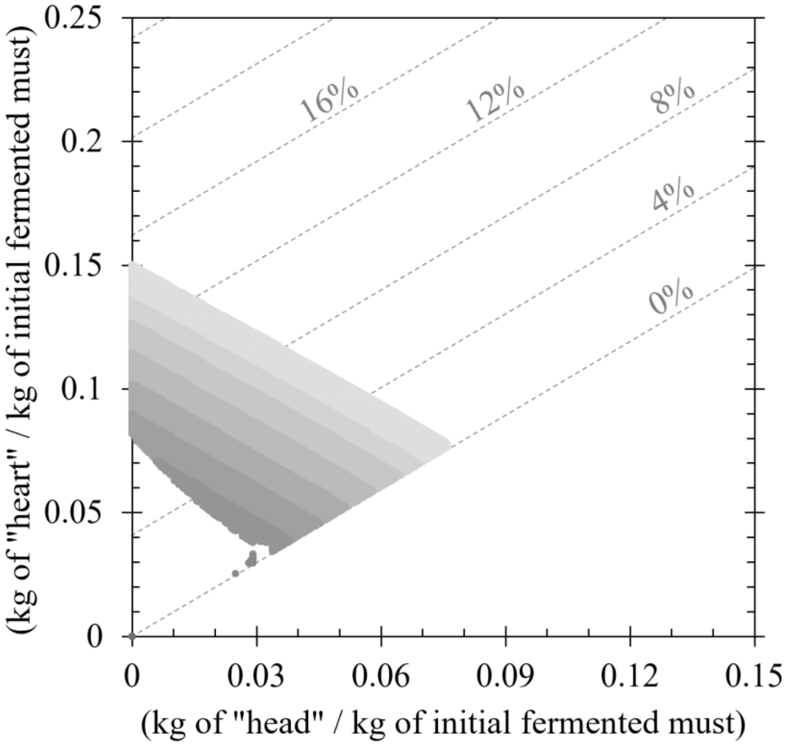

Figure 5. Characteristic curve of the cutting ranges. The axis x represents the "head", i.e., the first cut. The axis y represents the heart, i.e., the second cut. All the shaded regions represent distilling cut possibilities. The grey scale varied with ethanol concentration, from 38% (v/v) (light) to 48% (v/v) (dark), dotted lines represent the yields.

Figure 6 shows the possible distilling cuts to obtain *cachaças* with different ethanol concentrations without any other restrictions. The amount of ethanol, in the fermented must, determined the maximum number of cut possibilities and the maximum theoretical yield of the process (associated with the product obtained without cutting the head and with a maximum cut of the heart). Higher ethanol concentrations resulted in more possible distilling cuts with wider composition ranges, while lower ethanol concentrations resulted in a narrower composition range. The distilling cut representations, considering the minor compounds, are provided in the Supplementary Material (Figures S1–S16). Eight fermented musts (c16, c17, c18, c20, c21, c22, c23 and c24) did not allow any cut possibility resulting in a regular product. The results clearly showed the influence of minor compounds on yield and the several possibilities of final product composition and yield. The first cut (head) was not necessary to meet the composition specifications for several fermented must compositions.

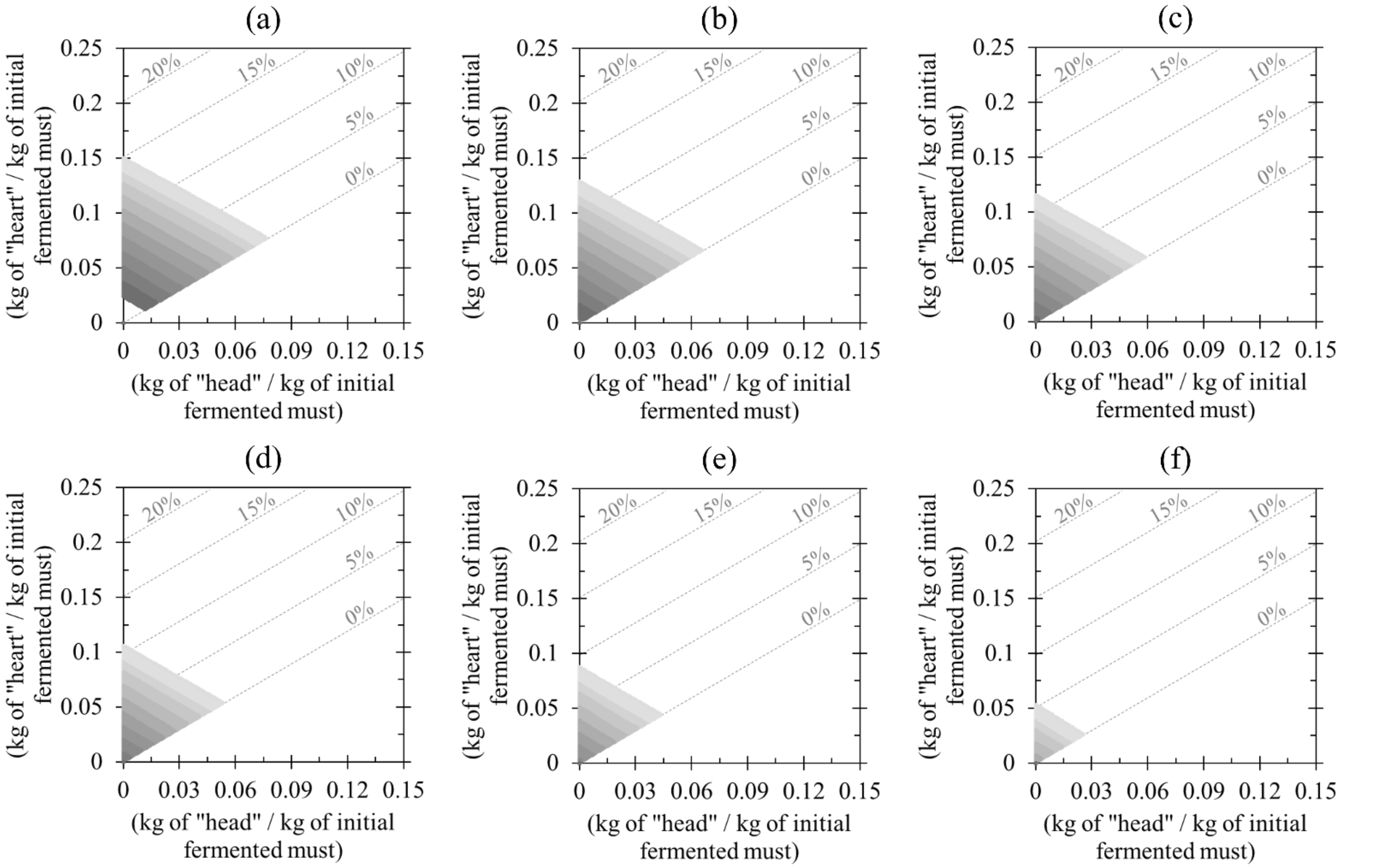

Figure 6. Cut ranges as a function of the ethanolic concentration of the distillate for each composition constructed without analyzing the concentrations of minority components. Fermented must (Mass fraction of ethanol): (**a**) c1 (7.25) (**b**) c7 (6.81) (**c**) c12 (6.54) (**d**) c16 (6.36) (**e**) c20 (6.00) (**f**) c23 (5.39). The grey scale varied with ethanol concentration, from 38% (v/v) (light) to 48% (v/v) (dark), dotted lines represent the yields.

Figure 7 shows the relationship between four minor compounds and ethanol concentrations. Acetaldehyde was the key compound influencing distilling cuts. All fermented must that did not present any distilling cut possibility possessed a high relation of acetaldehyde to ethanol. Fermented musts c4, c8 and c23 presented the same initial concentration of acetaldehyde (1.63×10^{-3} mg/mL), only c23 (which possessed a lower ethanol initial concentration) did not provide a regular product.

3.4. Influence of Minor Compounds on Spirit Quality

The presence of many important minor compounds in the process, such as methanol, the analysis of which was of major importance in this process, given its toxicity and its common presence in fermented sugar cane, was not identified in any fermented must reported by Oliveira et al. [22]. However, it is known that the presence of methanol in cachaça is a consequence of the hydrolysis of pectin from the sugarcane small bagasse fibers [18] and, therefore, of poor filtration and decantation after extracting the juice. Thus, these processes are essential to avoid excess of this substance in the broth.

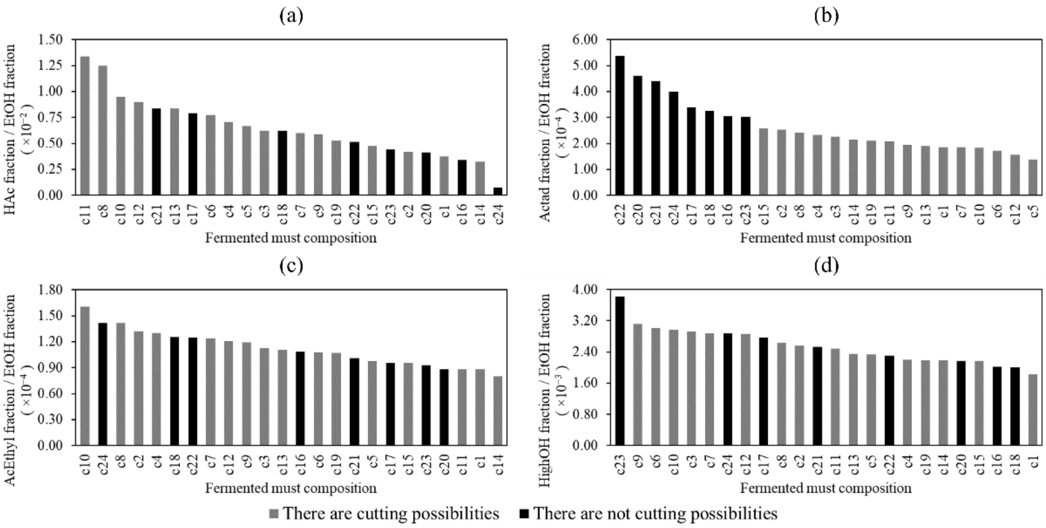

Figure 7. Ratio between mass fractions of the selected minor compound and ethanol (EtOH) in the fermented musts: (**a**) acetic acid, (**b**) acetaldehyde, (**c**) Ethyl acetate, (**d**) sum of higher alcohols (1-propanol + isobutanol + isoamyl alcohol).

To attest to the compounds' profile analyzed in the distilling cuts, different simulations were performed with fermented must compositions formed only by water, ethanol, and the minor compound of interest (acetic acid, acetaldehyde, ethyl acetate, or methanol) (Figure 8). The initial concentration of each minor compound was based on its c1 concentration and then gradually increased until the complete absence of cut possibilities. As the fermented must produced by Oliveira [22] did not contain methanol, the initial concentration was 0.002% (w/w), as reported by Campos et al. [40]. Although methanol can be controlled through good manufacturing practices before fermentation, its effect on distillation was analyzed due to its great toxic potential. Ethanol concentration was fixed at 9%, and water was determined by difference.

The increase in the acetic acid concentration did not influence the first cut. This increase also made the production of *cachaça* with high ethanol content necessary, resulting in a heavy compound, with prevalence in the last distillate fraction [26]. Both acetaldehyde and ethyl acetate compositions influenced the first cut, and the high concentration of these compounds was related to products with lower ethanolic content. This behavior was expected for intermediary compounds, with concentrations distributed between the distillation fractions. Methanol had more influence only in the second cut, considering products with high ethanol content. This behavior might suggest that methanol is a heavy compound. However, the volatility of minor compounds is influenced by the concentration of the two major compounds [37]. Methanol has volatility close to that of ethanol; depending on the ethanol concentration, methanol's volatility may be slightly lower (ethanol mass lower than 0.47) or slightly higher (high ethanol concentration region) than ethanol's volatility. This behavior is explained by the compensation of the ethanol activity coefficient in the dilution regions by the large values of methanol vapor pressure [1]. However, as widely known, methanol is a light compound, and thus, its presence was more prevalent in the head fraction. These results indicated that the congener limit was related to ethanol content and not to cachaça volume. The results were consistent with those observed in Figure 5, which matched previously reported ethanol relative volatilities.

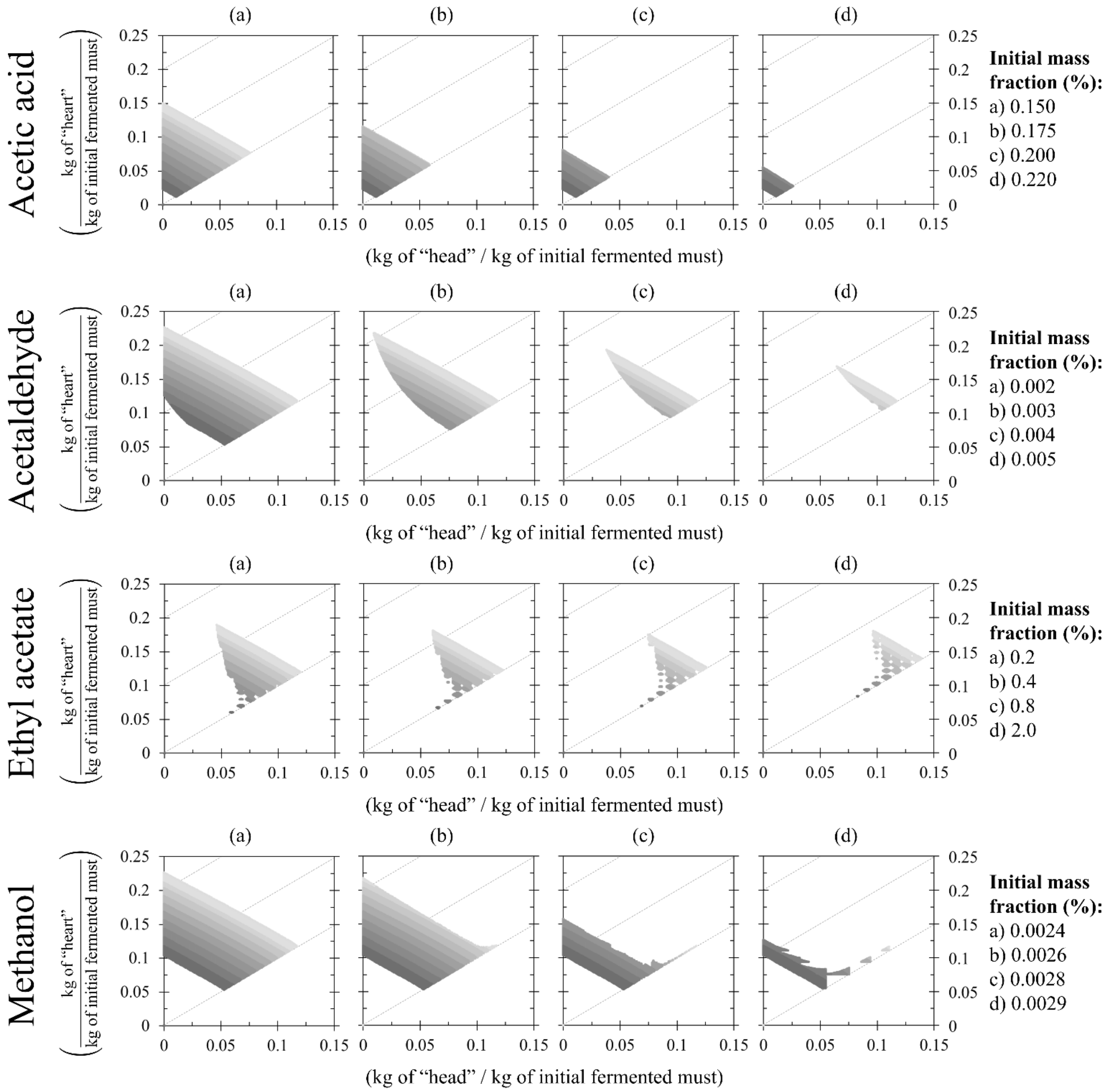

Figure 8. Cut ranges for the analysis of the influence of each minor component. The simulated fermented musts had compositions formed only of ethanol, and the substance of interest (varying, values in legend) and water (determined by difference). The grey scale varied from 38% (v/v) (light) to 48% (v/v) (dark), dotted lines represent the yields.

4. Conclusions

The results presented in this work show the relevance of considering the concentration of minor compounds in determining the cut ranges of the distillation of *cachaça*. The algorithm used in the computational simulation enabled the identification of countless distilling cuts, resulting in products with different alcoholic grades and process yields. Acetaldehyde was the key component to determine the possibilities of distilling cuts meeting *cachaça*'s legislation. However, more important than its concentration was the relation between acetaldehyde and ethanol. An increase in yield, compared to the traditional cut, of up to 3.7% in relation to the initial volume of fermented must was estimated, which represented more than 50% productivity gain. A previous analysis of the composition of fermented must and its respective possibilities of distilling may allow an improvement in the batch distillation process of *cachaça*. As a future work, the influence of the different fermented musts studied in this work on the parameters of continuous distillation should be investigated. Similarly, distillation of other spirits, such as whisky, pisco and rum, may be investigated.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr11010074/s1, Figure S1: Cut ranges depending on the alcoholic strength of distillate for composition c1; Figure S2: Cut ranges depending on the alcoholic strength of distillate for composition c2; Figure S3: Cut ranges depending on the alcoholic strength of distillate for composition c3; Figure S4: Cut ranges depending on the alcoholic strength of distillate for composition c4; Figure S5: Cut ranges depending on the alcoholic strength of distillate for composition c5; Figure S6: Cut ranges depending on the alcoholic strength of distillate for composition c6; Figure S7: Cut ranges depending on the alcoholic strength of distillate for composition c7; Figure S8: Cut ranges depending on the alcoholic strength of distillate for composition c8; Figure S9: Cut ranges depending on the alcoholic strength of distillate for composition c9; Figure S10: Cut ranges depending on the alcoholic strength of distillate for composition c10; Figure S11: Cut ranges depending on the alcoholic strength of distillate for composition c11; Figure S12: Cut ranges depending on the alcoholic strength of distillate for composition c12; Figure S13: Cut ranges depending on the alcoholic strength of distillate for composition c13; Figure S14: Cut ranges depending on the alcoholic strength of distillate for composition c14; Figure S15: Cut ranges depending on the alcoholic strength of distillate for composition c15; Figure S16: Cut ranges depending on the alcoholic strength of distillate for composition c19; Table S1: NRTL parameters for simulating batch distillation of fermented musts to produce *cachaça*.

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Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

NRTL	Non-Random Two Liquids model
HOC	Hayden O'Connell model
$w_{D,i}$	Mass fraction of distillate for compound i
w_i	Mass fraction of cachaça for compound i
C	Total amount of cachaça
D	Total amount of distillate
t_1	Time of first cut
t_2	Time of Second cut
AA	Anhydrous Alcohol
EtOH	Ethanol
Actad	Acetaldehyde
Isob	Isobutanol
Isoam	Isoamyl alcohol
AcEthyl	Ethyl acetate
Prop	1-propanol
HAc	Acetic acid
MetOH	Methanol
AAD	Average Absolute Deviation

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