

Wine Distillates: Practical Operating Recipe Formulation for Stills

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Consumer perceptions of flavors are associated with the chemical composition of foods. However, consumer preferences change; therefore, it is necessary for food manufacturers to be able to adapt their products. Unlike in aged spirits, the chemical composition of young spirits is determined during distillation; therefore, this is where distillers must tailor their operating recipes to the new trends. Even for an experienced distiller, the complexity of the process makes adapting the operating recipe far from straightforward. In this study, we developed a methodology for generating practical recipes that makes use of computer simulations and optimization techniques. We used *Pisco* Brandy, a young Muscat wine distillate from Chile and Peru as our case study. Even so, because our methodology is independent of the chemical composition of the broth, it can be applied throughout the industry. Drawing on the experience and preferences of industry enologists, we designed a preferred distillate and used our methodology to obtain the appropriate recipe. This recipe was validated in lab scale experiments, and we obtained a much closer distillate to the desired prescription than commercial products.

KEYWORDS: *Pisco* Brandy; ethanol; octanoic acid; linalool; dynamic optimization; dynamic modeling

INTRODUCTION

Most wine distillations (Cognac, Armagnac, and Brandy) can best be described as extractive and reactive batch distillation processes. The ethanol concentration determines the volatility of distillate aroma compounds. At the same time, many wine compounds are subjected to chemical reactions at low pH and high temperatures within the still.

The distillate ethanol concentration can vary widely during the process; therefore, how the still is operated will strongly influence both aromatic quality and productivity. Distillers simultaneously have to cope with complex process dynamics, the highly nonideal thermodynamic behavior of the mixture, multiple distillate fractions, coupled control variables, variations in wine composition, and also take into account changes in consumer preference.

Recent work on distilled spirits has focused either on aging and distillation system contributions to the final chemical composition of the spirit (1, 2) or on the relationships between this composition and the aroma and odor of the spirit (3–5). How distillation recipes affect spirit composition and the problem of adapting operation recipes to help distillers accom-

modate changes in consumer preference or cope with varying wine composition have received little attention though.

Computer simulation and optimization has proven successful in many areas of food and chemical processing. Such techniques have been applied widely in the field of batch distillation over the past 15 years. Most studies address still operation as an open-loop optimal control problem, where the goal is to maximize a specific performance index by finding the best control trajectories and switching times.

The most commonly used technique for solving batch distillation problems is the sequential approach (6–11) because of its simplicity. Here, a routine repeatedly integrates a set of differential-algebraic equations (DAE), representing the dynamic process, until an optimal solution is found. With relatively few decision variables and constraints, this strategy is effective. However, the method may fail to find a solution if there are too many decision variables. The sequential method really comes into its own once a reliable simulation has been developed, because then only a standard optimization routine is required to find the best control trajectory.

Alternatively, the simultaneous approach offers several advantages; the method is faster and can handle many more decision variables and constraints (12–14). The simultaneous approach does nevertheless require sophisticated optimization routines for handling large-scale problems as well as additional techniques to avoid numerical difficulties and to guarantee

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Table 1. Minor Compound Composition of the Artificial Wine

component	concentration (mg/L)
ethyl hexanoate	1.5
ethyl octanoate	1.0
methanol	278
<i>cis</i> -3-hexen-1-ol	2.6
isoamyl alcohol	206.6
octanoic acid	12.4
linalool	3.1
acetaldehyde	93.6

convergence. In this method, DAEs are discretized and transformed into nonlinear algebraic equations using orthogonal collocation on finite elements. These equations are coupled together with the optimization problem, leading to a single large-scale nonlinear programming (NLP) problem. The simultaneous approach has also been applied successfully to batch distillation optimization (15).

In this study, we report the result of many years of research aimed at developing a simple methodology for formulating precise recipes for operating stills. Distillers would benefit because they could obtain preferred standards for their products, which could be readily adapted to shifts in consumer preferences. Our method makes use of computer simulation and dynamic optimization, in which recipe formulation for still operation is tackled as an open-loop optimal control problem. The aim is to establish an operating routine to produce distillates that are both close to prespecified characteristics and enhance still productivity. As a case study, we applied our methodology to the distillation of *Pisco* Brandy, a young wine distillate from Chile and Peru that has a distinctive Muscat and fruity aroma. We validated the proposed methodology experimentally, at lab scale, using an artificial wine containing a reduced set of volatiles that covered the entire spectra found in freshly distilled *Pisco* Brandy (16).

MATERIALS AND METHODS

Process Description. Wine is a complex mixture, exhibiting highly nonideal thermodynamic behavior, and comprises water, ethanol, colloids, fining agents, and between 600 and 800 distinct volatile compounds in a total concentration of 1.0 g/L (17, 18). In the distillation process, volatile species from wine are extracted and concentrated. Although a distillate or spirit is mainly water and ethanol (up to 98 wt %), its aroma is the upshot of many trace volatile species that we shall refer to here as minor compounds. It is the relative concentration of these minor compounds that essentially defines distillate quality. This work focuses on the distillation of *Pisco* Brandy, a wine distillate from Chile and Peru with a distinctive Muscat aroma that is mainly attributable to its high terpene content (19). *Pisco* Brandy is manufactured in a still consisting of a reboiler, a rectification column (optional), a partial condenser, and a total condenser. Reflux occurs by removing heat from the partial condenser. Hence, operating variables for the still are the partial condenser cooling rate and the reboiler duty.

The distillate is traditionally divided into three fractions, denoted as the head, heart, and tail. The heart is processed further to produce *Pisco*, while the head and tail fractions are separated and redistilled later. On an industrial scale, this process is handled manually according to heuristic operation recipes in 1500 L stills.

Artificial Wine. An artificial wine mixture was used for the experimental runs. A concentrated solution was prepared containing the minor compounds for the three distillation runs to minimize variations in the initial wine composition. Just before each distillation, one-third of the concentrate was combined with 10.4 L of an artificial wine matrix (20). **Table 1** shows the initial composition of the minor compounds in the resulting artificial Muscat wine. These values correspond to average concentrations found in real Muscat wines analyzed in our lab.

Chemical Analysis. Samples of the initial wine, residual waste wine, and accumulated distillate fractions were taken for analysis of chemical composition using gas chromatography. The alcoholic grade of each sample was calculated from literature tables (21) based on temperature-corrected density measurements. Sample density was measured at 20 °C using a picnometer and a high precision balance.

Distillate samples were diluted with water to 20 °GL (the artificial wine and the residual waste wine were not diluted) and separated in three flasks, each with 100 mL of sample; 100 μ L of an internal standard was added (3.6 mg/mL 4-nonanol). Volatiles from the samples were isolated, in two extraction steps, with dichloromethane (25 mL per 100 mL of sample) in a N₂ environment, at low temperature, agitated for 30 min, separated in a centrifuge, and then concentrated by distillation (22). To identify and quantify volatile compounds, 2 μ L of the concentrated solution was injected into the GC-MS (Hewlett-Packard 6890 GC) equipped with a split/splitless injector, a polar polyethylene packed column (30 m \times 0.25 mm i.d.; 0.25 bonded phase, HP-FFAP) and a mass spectrometer (HP 5972). The mass detector temperature was 280 °C. The initial injector temperature of 60 °C was held for 3 min and then increased at a rate of 3 °C/min to a maximum of 235 °C where it was sustained for 5 min. Concentrations of minor compounds were calculated from the relative response areas of each volatile to the internal standard (23). Calibration curves were prepared by GC-MS analysis of extracts of a model hydroalcoholic solution (20 °GL) containing known amounts of the minor compounds analyzed (ethyl hexanoate, ethyl octanoate, *cis*-3-hexen-1-ol, isoamyl alcohol, octanoic acid, linalool, and acetic acid) and the internal standard (4-nonanol). Calibration curves were all linear, with r^2 higher than 0.99 in all cases. From the above procedure, we compared the concentrations of minor compounds against two model solutions with different known compositions and derived the corresponding correction factors for each compound accordingly.

Recipe Formulation. The method that we developed to formulate the operation recipe for wine stills involves several stages:

- Develop a batch distillation model able to reproduce the experimentally observed recovery of volatile aromatic compounds.
- Establish a preferred distillate according to the aroma preference of a given consumer group and express this preference in terms of the fewest possible volatile compounds.
- Define a measure of how close we are to the preferred spirit, in terms of a mathematical objective function.
- Formulate and solve an NLP problem that will provide a recipe (control trajectory) for operating the still.

Now we provide details on how we implemented each stage.

Process Model. The wine still operation was modeled as a nonideal multicomponent, multiple-fraction, reactive batch distillation process (24). The mathematical model (see the Supporting Information for more details) includes dynamic mass and energy balances for each tray, with nonideal vapor-liquid equilibrium and reaction kinetics that were fitted from experimental data. Mass transfer is modeled by introducing the Murphree tray efficiency, considered constant for every tray. The model assumes constant pressure through the column, perfect mixing on each tray, no accumulation in the vapor phase, and a negligible influence of minor compounds in the physical and thermodynamic properties of the mixture (density, enthalpy, and boiling temperature). All heat losses are included in the model but grouped in the partial condenser model. These conditions provide a set of differential and algebraic equations (DAEs) that is solved for the entire operating period of the still. For solving the model equations, we used an efficient functional approach that converts the set of DAEs into a simpler ordinary differential equation (ODE) system, which was achieved by transforming the implicit set of algebraic equations into an explicit artificial neural network (24).

Preferred Distillate. The chemical composition of the distillate determines the most important factor of quality in the product, the spirit's aroma. For *Pisco* Brandy, however, investigation into the relationship between composition and aroma is still ongoing, and while a number of promising advances have been made (19, 25, 26), as of now, there is no clear-cut agreement on the optimal composition of *Pisco*. Therefore, we had to rely on the experience and preferences of enologists working in the *Pisco* industry to establish our preferred

distillate. In a freshly distilled *Pisco*, they look for a strong Muscat aroma that is not impaired with tails.

A standardized set of sensory terms for *Pisco* has recently been developed (27). Here, the sensory panel most frequently used the descriptor linalool. In another study, a set of chemical markers has been proposed to track the sensory contributions of all postfermentation processes in *Pisco* production (26). Molecular linalool was considered a suitable chemical marker for tracking linalool aroma in freshly distilled *Pisco* Brandy. Moreover, it is well-known that monoterpene compounds such as linalool, nerol, and geraniol are the terpenols that most determine the distinctive Muscat aroma (28). In freshly distilled *Pisco*, on average, linalool is found in concentrations 10 times higher than in other wine distillates such as freshly distilled Cognac (4, 16). Returning to freshly distilled *Pisco*, the sensory descriptor tails correlates well with octanoic acid (26). Therefore, in line with the preferences of the *Pisco* enologists consulted, our preferred distillate should contain high concentrations of linalool and low concentrations of octanoic acid.

Objective Function. The literature contains many formulations of objective functions for batch distillation, which can be classified into three broad groups: minimum time (9, 29), maximum distillate (6, 10, 13), and maximum profit (7, 11). None of these, however, can be easily adapted to provide a good measure of how close we are to the ideal freshly distilled *Pisco* as just described. Hence, we proposed a multiobjective cost function with adjustable weights that entails both linalool recovery (associated with the characteristic aroma of *Pisco*) and octanoic acid recovery (associated with tails aroma). In addition, we built in the cost function ethanol recovery; *Pisco* enologists also have to be concerned about productivity. We define recovery in eq 2. Finally, to simplify adjustable weight tuning, recoveries were normalized by the maximum possible recovery that can be attained during the corresponding distillation stage. The objective function can therefore be written as

$$J = \alpha \left(\frac{\text{REC}_{\text{eth}}(t_f)}{\text{MaxREC}_{\text{eth}}} \right) + \beta \left(\frac{\text{REC}_{\text{lin}}(t_f)}{\text{MaxREC}_{\text{lin}}} \right) - \gamma \left(\frac{\text{REC}_{\text{ocac}}(t_f)}{\text{MaxREC}_{\text{ocac}}} \right) \quad (1)$$

$$\text{REC}_j = 100 \frac{\int_{t_i}^{t_f} (D(t)x_j(t))dt}{M_0 x_j(t_i)} \quad j = \text{eth, lin, and ocac} \quad (2)$$

$$\alpha + \beta + \gamma = 1 \quad (3)$$

Here α , β , and γ are adjustable weights; REC_j is the recovery of compounds j (eth = ethanol, lin = linalool, and ocac = octanoic acid); $D(t)$ is the molar flow rate of the distillate; x_j is the mole fraction of species j ; M_0 is the initial batch charge; and t_i and t_f are the initial and final distillation times, respectively.

Because the composition of the distillate stream varies widely during the batch, to simplify the optimization problem, we divided the heart fraction of the distillate into two subfractions, an initial aromatic fraction (IAF) where most of the linalool is recovered and a second neutral fraction (SNF) where most of the ethanol is recovered, optimizing the two separately with different adjustable weights. Splitting the heart into two would also make it easier for the enologist to adapt the product to consumer preferences, because different proportions of the heart could be used during the blending of the final *Pisco* Brandy.

Because the preferred distillate should contain high concentrations of linalool and low concentrations of octanoic acid, the weight parameters, β and γ , in IAF, were set at 0.5, meaning that linalool recovery should be high and octanoic acid recovery should be low. In the SNF distillate, we need to recover as much ethanol and as little octanoic acid as possible. Tuning the objective function weights here was awkward, because balancing productivity and octanoic acid composition proved tricky. We tested different weights, but we either achieved undesirably low ethanol recoveries or too much octanoic acid. Finally, we set $\alpha = 0.8$ and $\gamma = 0.2$ and added two constraints to the optimization problem: ethanol recovery must reach at least 45%, and the octanoic acid concentration in the distillate should be lower than a prespecified value.

Formulation and Solution of the Optimization Problem. After standard practice in the *Pisco* industry, we chose the cooling rate in

the partial condenser, q_{out} , as the control variable and used a predefined trajectory for the reboiler duty to keep the distillate flow rate above a minimum (10 mL/min). Thus, the optimization procedure needs to find a cooling rate trajectory that maximizes the objective function (eq 1) for a given set of weights. The cut time between IAF and SNF was set at 22 min, from our experience, to ensure that IAF is not impaired with tails aroma. The final time was set at 80 min, because the octanoic acid concentration in the distillate rises to undesirable levels afterward.

The head fraction (from the first 3 min of distillation) was not optimized; the standard *Pisco* industry practice is to operate this stage using minimum cooling. Instead, the head fraction was simulated in advance, and the outcome was taken as the initial condition for the distillation model used in the optimization. Aside from the upper and lower bounds for the control variable, no additional constraints were considered in the optimization for the IAF distillate. Two additional constraints were included, however, for the optimization of the SNF distillate to ensure a minimum ethanol recovery and a maximum octanoic acid concentration.

The optimal control problem that we describe is of infinite dimension, because the control variable, q_{out} , is a function of time and not just a single value. Hence, to find a practical solution, the control vector must be expressed as a function of a reduced set of control parameters. Instead of using standard approximations, such as linear or piecewise constant functions for multiple control intervals, here, we used a heuristically derived exponential function, $u(t)$, representing the trajectory of the control variable ($q_{\text{out}}(t)$ in our case)

$$u(t) = u_f - \frac{k}{k-1}(u_f - u_i)(1 - k^{((t-t_i)/(t_f-t_i)-1)}) \quad (4)$$

$$\mathbf{z} = [t_i, t_f, u_i, u_f, k]^T \quad (5)$$

where the vector \mathbf{z} , representing the control parameters in the optimization, includes the parameters that specify the control trajectory. Therefore, for our case study, as the initial and final times are known, just three parameters need to be specified by the optimization procedure: initial (u_i) and final (u_f) values of the control variable and the curvature constant (k). The continuous function chosen (eq 4) was developed in lab experiments to generate a wide variety of smooth and feasible control profiles. This function narrows the selection of $u(t)$, both greatly simplifying optimization calculations and improving simulations stability, but it may not represent the optimal trajectory.

Thus, the optimal control problem can be stated as follows:

$$\max_{\mathbf{z}} J(\mathbf{z}) \quad (6)$$

subject to the constraints

$$\mathbf{f}\left(\frac{d\mathbf{x}(t)}{dt}, \mathbf{x}(t), \mathbf{z}, t\right) = 0 \quad (7)$$

$$\mathbf{g}(\mathbf{x}(t), \mathbf{z}, t) \leq 0 \quad (8)$$

$$\mathbf{z}_{\text{min}} \leq \mathbf{z} \leq \mathbf{z}_{\text{max}} \quad (9)$$

where \mathbf{f} , the vector of ODEs, and \mathbf{g} , the vector of algebraic inequality constraints, are defined by the dynamic process model (see the Supporting Information) and the specific optimization constraints introduced by the user (as discussed above). In addition, \mathbf{x} represents the vector of state variables, and \mathbf{z} represents the vector of control parameters.

We solved the above optimal control problem using a sequential optimization approach within MATLAB, as shown in Figure 2. An important advantage of this approach is that it is straightforward to implement if an accurate simulator of the process is already available, which it was in our case. The process model was integrated using the ODE15s "stiff" integration routine, and FMINCON, an iterative sequential quadratic programming (SQP) algorithm, performed the optimization. FMINCON calculates values of the objective and constraint functions along with numerical approximations of their gradients.

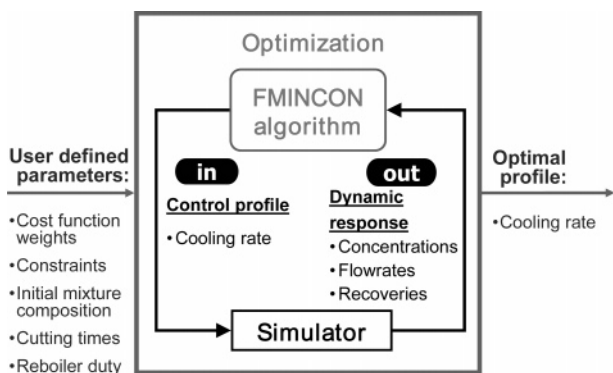


Figure 1. Recipe formulation method. The user provides problem constraints and objective function weights. The optimization routine (FMINCON) guesses a cooling rate profile, which is tested in a simulation of the distillation process. The outputs of the simulation (ethanol, octanoic acid, and linalool recoveries) are used to compute the value of the objective function, and based on this and the gradients of the constraints, the objective function proposes a new cooling rate profile. The procedure is repeated until no further increment in the objective function is achieved.

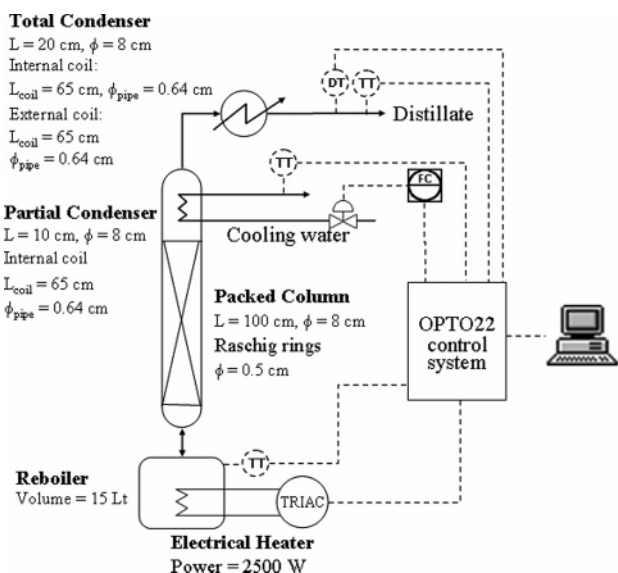


Figure 2. Process and Instrumentation Diagram (P&ID) of the lab scale distillation still used in our experiments. DT, density sensor; TT, temperature sensor; FC, flow controller.

We reduced the number of mixture components during the optimization procedure by including only the minor compounds that take part in the objective function. This resulted in reliable optimization, with reasonably short computing times (from 3 to 28 min on a Pentium III 700 MHz PC). The optimization procedure was repeated 5 times using different control variable starting values to avoid local optima.

Experimental Apparatus. Our distillation experiments were carried out in an automated batch still, made of 316 stainless steel and was thermally insulated with a 4 cm layer of mineral wool. As shown in **Figure 1**, the still consisted of a 15 L reboiler, powered by electric heaters, connected to a distillation column packed with glass Raschig rings providing a similar separation capacity to that found in many industrial *Pisco* Brandy stills. The partial condenser, located at the top of the column, was a vertical heat exchanger containing a coil refrigerated with water to produce the liquid reflux stream. The total condenser was a heat exchanger with internal and external coils connected in series. The still was equipped with an OPTO-22 SNAP LCSX PLUS data acquisition and control system. A Pentium II PC provided the user a graphical interface to operate the column and stored historical data. The ethanol concentration of the distillate was measured using an Anton-Paar L-Dens density transmitter with temperature compensation. Cooling water flow rate in the partial condenser was

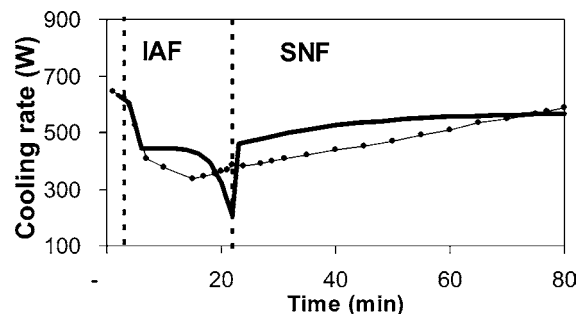


Figure 3. Cooling profiles for the new and traditional operating still recipes. New recipe (—), traditional recipe (---), corresponding to the constant ethanol concentration at 75%.

Table 2. Recoveries Using Improved and Traditional Recipes from Simulation

fraction	compound	improved (%)	traditional (%)
IAF	ethanol	26.0	25.9
	linalool	80.0	80.6
	octanoic acid	0.5	1.0
SNF	ethanol	43.8	44.7
	linalool	12.2	12.6
	octanoic acid	2.1	8.1
total heart	ethanol	69.8	70.6
	linalool	92.2	93.2
	octanoic acid	2.6	9.1

manipulated using a modulating solenoid valve, DANFOSS EVSIM 6. Finally, a TRIAC circuit modified the voltage applied to the electric heater in the reboiler.

In the experimental runs, we used the alcoholic degree in the distillate (obtained from the simulation with the optimal recipe) as a varying set point to be tracked by a Fuzzy control strategy, similar to one described in ref 30. Here, the valve opening of the cooling water in the partial condenser was used as the manipulated variable. This produced more reliable results than tracking the cooling rate directly. The same distillation recipe was performed 3 times. However, only two distillations were analyzed because one was saved for verification in the event of severe discrepancies in the results. The initial charge for each run was 10 L (498.6 mol), and the initial composition of the mixture was the one measured in the obtained artificial Muscat wine, as described above (**Table 1**).

RESULTS AND DISCUSSION

Comparing the New Recipe with a Traditional Recipe via Simulations. We simulated the entire distillation and followed the optimal control profile once the optimal solution was found for each fraction. Simulation of the optimal recipe was compared with a simulation of a traditional distillation recipe (**Figure 3**), typically applied by industrial *Pisco* distillers. **Table 2** displays the simulation results. In the first fraction, IAF, both recipes achieved similar recoveries of ethanol and linalool; however, the traditional recipe recovered twice as much octanoic acid as the formulated recipe. In the SNF, the traditional recipe recovered slightly more ethanol but 4 times as much octanoic acid. For the entire distillation, the traditional recipe recovered 3 times more octanoic acid but without significantly raising the levels of ethanol or linalool. The new recipe, given by the cooling rate trajectory shown in **Figure 3**, is far from obvious and would hardly be derived from the process experience alone.

Experimental Validation. Lab scale experiments confirmed that it is possible to recover high amounts of linalool and low amounts of octanoic acid simultaneously. Using the new recipe, IAF distillates contained much more linalool and less octanoic acid (**Table 3**) than reported for the first heart fraction in

Table 3. Comparison between Industrial and Lab Scale Still Distillates for Both Heart Fractions^a

	linalool	octanoic acid
experimental IAF	67 ± 5	5.5 ± 0.5
maximum industrial still ^b	22.4	23.3
minimum industrial still ^b	15.4	7.2
experimental SNF	10.7 ± 0.9	23 ± 2
maximum industrial still ^b	6.2	39.3
minimum industrial still ^b	3.4	7.9

^a Concentrations in mg/L of absolute ethanol. ^b Taken from ref 26.

Table 4. Comparison between Complete Heart Distillate in Lab Still and Commercial *Piscos*^a

	linalool	octanoic acid
simulation	28.8	1.3
experimental	26 ± 2	18 ± 2
maximum composition ^b	18.2	43.8
minimum composition ^b	0.0	14.9

^a Concentrations in mg/L of absolute ethanol. ^b Taken from ref 26.

Table 5. Simulated and Experimental Recoveries in Fractions IAF and SNF and in the Total Heart

fractions	compound	simulation (%)	experimental (%)
IAF	ethanol	24	17.5 ± 0.4
	linalool	75.2	59 ± 6
	octanoic acid	0.4	0.9 ± 0.1
SNF	ethanol	45.4	43.2 ± 0.6
	linalool	15.4	25 ± 3
	octanoic acid	1.8	9.3 ± 0.8
total heart	ethanol	69.4	60.7 ± 0.5
	linalool	90.5	84 ± 9
	octanoic acid	2.3	10.2 ± 0.9

industrial stills (26). In the resulting SNF distillate, the octanoic acid concentration was similar to the average observed in industrial stills (26), but we recovered twice as much linalool (Table 3).

Our final distillate, obtained from blending the entire IAF and SNF fractions, was more concentrated in linalool than any recently evaluated commercial *Pisco* (Table 4). The lab scale distillate also contained less octanoic acid than the average in these commercial spirits (26).

Model Accuracy. For the purposes of formulating a practical operating recipe, our model was sufficiently accurate to produce a superior distillate compared to commercial *Pisco* Brandies. The model is accurate for predicting ethanol and linalool recoveries, taking into account measurement errors and deviations induced by the limitations of the experimental system (on average around 10% overall errors). The linalool concentration, for example, in our final distillate was only 3 mg/L lower than predicted (Table 4).

As shown in Table 5, linalool recovery was 16% lower than predicted in the IAF distillate but 10% higher in the SNF distillate, and thus overall, the recovery was 7% lower than predicted. Ethanol recoveries, in turn, were just 7 and 2% lower than predicted in the IAF and SNF distillates, respectively; the overall recovery in the final distillate was 9% lower than predicted.

Although the model predicted correctly that virtually no octanoic acid would be recovered in the head (not shown) and that the initial fraction would contain just a small amount (Table 5), our prediction of octanoic acid recovery in the SNF distillate

Table 6. Effect of Cutting Time on Recoveries in the IAF Fraction

final time (min)	ethanol (%)	linalool (%)	octanoic acid (%)
18	21.3	74.1	0.43
20	23.5	77.1	0.47
22	25.7	79.6	0.50
24	28.0	81.2	0.53
26	30.0	83.4	0.56

was 5 times lower than experimentally observed. The octanoic acid concentration in the final distillate was much higher than predicted too (Table 4). The latter is probably due to the high and increasing acidity of the boiling mixture, which affects the complex equilibrium of the dissociated and nondissociated forms of this organic acid in the aqueous solution. A better thermodynamic model for octanoic acid needs to be developed to attain improved predictions. While the recovery of octanoic acid is higher than predicted, because of experimental volatilities that are 2–3 times higher than our models predicted for every control trajectory, we presume that the obtained recipe will be the same.

Sensitivity to Cutting Times. On the basis of previous experience, for the above results, the cutting time between the IAF and SNF distillates was set to 22 min. This apparently arbitrary decision could restrict the performance of the distillation. Consequently, a sensitivity analysis of the optimal solution was performed with respect to the cutting time, applying the same optimization procedure, objective function, initial wine composition, and evolution of the reboiler duty as described earlier. Four different final times were evaluated, 18, 20, 24, and 26 min, and compared to the original cutting time (Table 6). Sensitivity results showed that, as the final time increased to 26 min, it was possible to recover more ethanol and linalool without recouping significantly more octanoic acid. Table 6 also shows that ethanol recovery was more sensitive to cutting times than linalool and octanoic acid recoveries. For example, for a cutting time of 26 min, ethanol recovery increased 16%, while linalool recovery increased 7%, compared to the amounts recovered after the nominal cutting time of 22 min.

Lab scale experiments validated the methodology that we propose for formulating practical though nonintuitive wine-still operating recipes. The optimization methodology that we describe here can be adapted to include the reboiler duty as a control variable, additional cuts, and more constraints and also to find optimal cutting times. However, these adjustments would increase the computing time needed and may cause the optimization to fail to converge. Should greater flexibility be required, we recommend using the alternative simultaneous optimization-solution approach together with a robust optimization solver for large scale systems (14). Because our methodology is independent of the chemical composition of the fermented juice, it may be employed to produce any distilled spirit.

ABBREVIATIONS USED

DAE, differential algebraic equation; IAF, initial aromatic fraction; NLP, nonlinear programming; ODE, ordinary differential equations; SNF, second neutral fraction.

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Supporting Information Available: Reactive batch wine distillation model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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