

Modeling and Prediction of Evaporative Ethanol Loss During Wine Fermentations

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A kinetic model for batch alcoholic fermentations, such as those employed in winemaking, has been modified to calculate evaporative losses of ethanol. Computer generated solutions exhibit good agreement with reported experimental measurements. The model is used to illustrate the effects of inoculum level, sugar utilization, must temperature, non-isothermal conditions and cap temperature on evaporative ethanol losses. A master correlation is presented for estimation of losses under any combination of temperature and sugar utilization during entire, isothermal batch fermentations.

Recent actions by regulatory agencies indicate a move toward classifying ethanol as a high reactivity photochemical pollutant with very little technical substantiation. The perceived need to quantify evaporative losses during wine fermentations has led to significant expenditures on large-scale fermentor emission measurements. A much more efficient, versatile, and useful approach is to employ computer fermentation modeling to predict evaporative losses under any set of fermentation conditions. The results of this approach are presented below.

The question of evaporative losses of ethanol during wine fermentations and proposed methods of recovery has been a subject of interest in the enology literature since as far back as 1821 when Gay-Lussac addressed the problem (8). Several authors have reviewed the literature (1,14,16,18), some of which is replete with both theoretical and experimental error.

dimensions for the ordinate which indicates that the reported ethanol losses range from 0.1 to 1.5 percent by volume (% vol/vol). This can only be interpreted to mean the expected decrease in wine ethanol concentration (% vol/vol) due to losses during fermentation. In fact, the original data they have plotted from the literature express the loss in terms of ethanol lost as a percent of ethanol formed. This quantity is independent of the dimensions of ethanol concentration. The ordinate of their plot should read "Ethanol lost as a percentage of ethanol formed." The actual decrement in wine ethanol (% vol/vol) would be approximately a factor of ten smaller. Thus, actual wine alcohol content decreases should range from 0.01 to 0.15 percent by volume (% vol/vol).

In addition, Ough and Amerine (12) have assumed that the initial sugar concentrations (°Brix) were completely fermented. This was almost correct in some of the

Table 1. Summary of literature results on ethanol losses.

Reference	Year	Vessel size L	Temperature °C	Sugar		Ethanol formed		Ethanol lost		Ethanol lost as percent of ethanol formed
				Initial g/L	Used g/L	% vol/vol	g/L	% vol/vol	g/L	
10	1946	—	22	216 (a)	216	10	79	0.06	0.47	0.6
7	1949	2.5	35	182	180.3	10.85	85.6	0.13	1.03	1.2
			20	182	180.0	10.82	85.2	0.07	0.55	0.65
			5	182.8	179.4	10.84	85.5	0.02	0.15	0.18
5	1951	4000	27-30	204	202.2	12.1	95.5	0.06	0.52	0.54
16	1963	10	26-28	—	265 (b)	13.21	104.2	0.11	0.86	0.83
		284091	29-31	—	115 (b)	6.07	48.0	0.07	0.56	1.17
18	1964	2-16	10	220	220 (c)	11.2 (b)	88.5	0.012	0.097	0.11
			21	220	220 (c)	11.2 (b)	88.5	0.053	0.416	0.47
			21	276	240 (c)	12.1 (b)	95.5	0.07	0.554	0.58
			21	276	240 (c)	12.1 (b)	95.5	0.086	0.678	0.71
			26.5	220	220 (c)	11.2 (b)	88.5	0.073	0.575	0.65
			32	220	220 (c)	11.2 (b)	88.5	0.10	0.796	0.90
			34	276	240 (c)	12.1	95.5	0.165	1.30	1.36
6	1974	121120	27-32 (c)	—	177 (d)	10.8	85.6 (d)	0.009	0.07	0.083
11	1980	340909	11.3	160	140	7.3	57.6	0.023	0.18	0.313

a. Calculated assuming 20°Brix yields 10% vol/vol ethanol.

b. Calculated assuming 1°Brix yields 0.55% vol/vol ethanol.

c. Estimated from the original reference.

d. Calculated from CO₂ production.

Ough and Amerine (12), and more recently, Amerine and Ough (2), have presented graphical illustrations which summarize reported values of ethanol losses from the literature. However, their graphs are in error and contribute to the confusion. The major error concerns the

reported cases, but not in others. In addition, they normalized all of the experimental values of ethanol loss, obtained with diverse values of °Brix, to a standard value of 22.5°Brix. This was done assuming direct proportionality between ethanol loss and initial °Brix. It can be easily shown mathematically (17) that this assumption is only correct if loss is expressed as a percentage (or fraction) of formation for an entire isothermal juice

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Manuscript submitted for publication 29 March 1983.

fermentation. Therefore, the assumption was correct for the actual data they were attempting to adjust. However, if loss is expressed as the decrement in liquid phase ethanol concentration (% vol/vol, % wt/wt, or g/L), which their graph erroneously suggests for the data, then direct proportionality does not apply. In this case, for entire isothermal juice fermentation, the ratio must employ the second powers of the respective sugar concentrations utilized (or the second power of initial °Brix, assuming complete fermentation)(17).

A complete tabulation of reported literature values for ethanol loss during fermentation is presented in Table 1. All pertinent information is given, either from the original literature, or else it has been calculated or assumed as specified in the table's footnotes. It can be seen that the values of wine ethanol (% vol/vol) loss range from 0.012 to 0.165 % vol/vol. The values of ethanol loss, as a percentage of ethanol formation, range from 0.11 to 1.36 percent.

Materials and Methods

The model: The computer model used in this work (17) is built upon the fermentation kinetic model of Boulton (3,4). This model assumes that the only important mechanism for ethanol loss is equilibrium evaporation into the escaping CO₂ stream. Physical entrainment of small droplets was shown to be insignificant in modern closed fermentation vessels (17). The careless use of the term "entrainment" by some authors (16,18) has perhaps derived from the French meaning. In modern engineering terminology, entrainment can only mean actual suspension of small liquid droplets in a gas. Although such droplets are readily formed, their escape from closed vessels should be insignificant.

Reliable recent experimental data (13) for pure ethanol-water mixture phase equilibrium thermodynamics were fitted to functions in the regions of temperature (0-40°C) and ethanol concentration (0-14% vol/vol) which pertain to wine fermentations. Although actual data for fermenting musts and wines or their model solutions, which contain considerable amounts of dissolved sugar and other solids, would be preferable, such data are not available. This information was incorporated into the fermentation model to allow calculation of ethanol and water vapor concentration in the CO₂ stream. The model calculates the rates of loss throughout the fermentation and integrates these rates to give the total amount lost. The model has been used to verify experimental measurements made in the past and to predict ethanol losses for a variety of cases based on changes in fermentation conditions which are under the control of the winemaker.

A typical result of the computer simulation for a 20°Brix juice at 21.1°C is shown in Figure 1. This figure displays not only the liquid phase sugar and ethanol concentrations, but also the vapor phase ethanol concentrations in the CO₂ stream. In addition, the rates of CO₂ evolution and ethanol evaporative loss are shown. The areas under the two bell-shaped rate curves correspond to the total CO₂ produced and the total ethanol lost, respectively. It may be seen that the maximum rate of ethanol

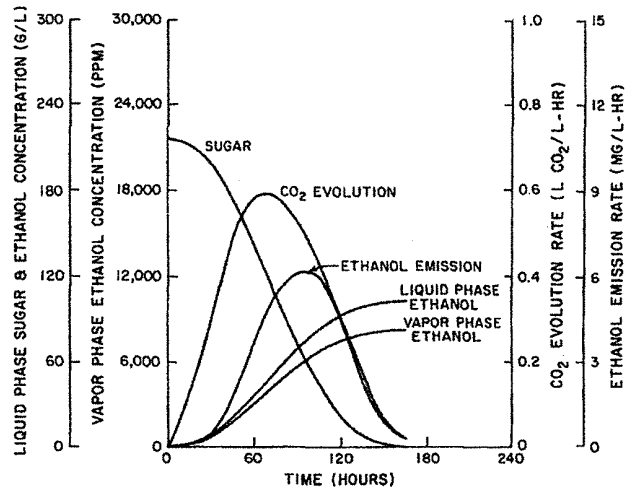


Fig. 1. The predicted rates of CO₂ evolution and ethanol emission and liquid and vapor phase ethanol concentrations. (Initial sugar content of 20°Brix, isothermal T=21.1°C.)

loss does not coincide in time with the maximum rate of CO₂ production, which corresponds to the maximum fermentation rate. This result clearly refutes the arbitrary assumption that maximum ethanol loss occurs simultaneously with maximum fermentation rate (12). Although not typical of most wine fermentations, this case results in a vapor phase ethanol concentration of 8300 ppm, a maximum CO₂ production rate of 0.6 liters per liter of must per hour and a maximum ethanol loss rate of 6 mg/L of must/hour. Total ethanol loss was 475 mg/L or 3.96 lb per 1000 gallons.

Results and Discussion

Model validation: The model has been used to fit sugar depletion curves reported in the literature. Once an acceptable fit is obtained, a comparison of other predicted quantities, with their measured values should indicate the degree of validity of the model.

In one case, an industrial scale (90 000 gallons) measurement by a regulatory agency (11) was modeled (Fig. 2). The irregular sugar depletion curve was fitted approximately, and the resulting predicted vapor phase ethanol concentration compared reasonably well with the measured values, especially later in the fermentation when most of the sugar is used up. The disparity early in the fermentation is due partly to under-estimation of sugar depletion (and thus liquid phase ethanol concentration) with this particular fit. In addition, the high sugar concentration initially present probably exerts some effect on increasing the ethanol activity coefficient (and therefore, partial pressure). This effect could be built into the model as well if the experimental data were available.

The ethanol emission rate curves in Figure 2 predicted by the model and measured experimentally differ somewhat from one another, being close in magnitude but not coinciding in time of peak occurrence. Such rate curves are very sensitive to the exactness of fit of the sugar depletion curve, so this small disparity is not

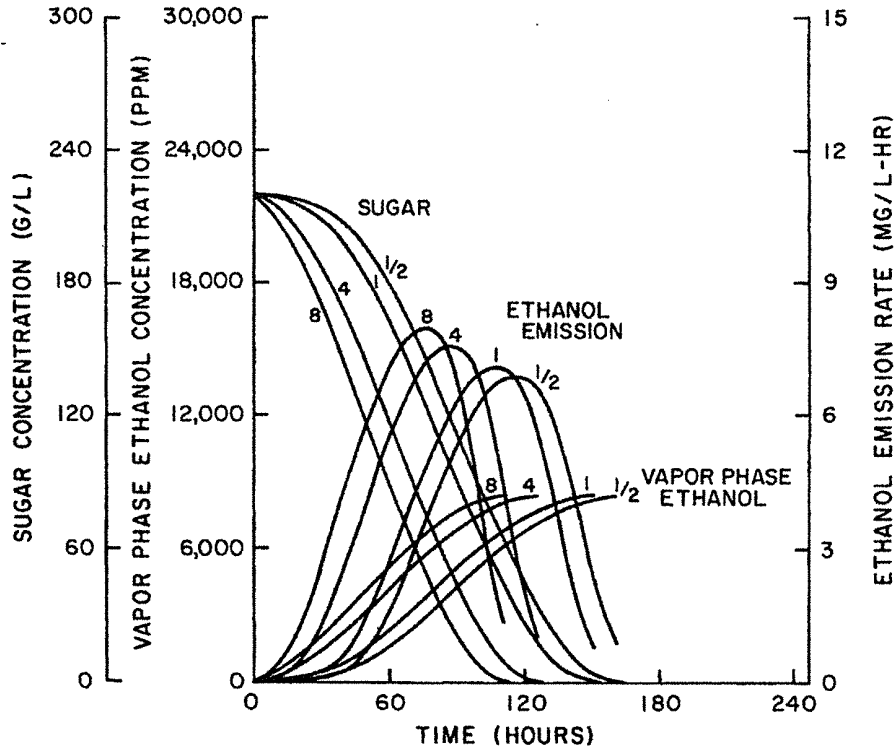


Fig. 4. The influence of initial inoculum level on the rate of fermentation, the rate of ethanol emission and the vapor phase ethanol concentration. (Initial sugar content of 20°Brix, isothermal T=21.1°C.)

appreciated by previous workers. In a recent paper covering theoretical aspects (17), it has been shown that ethanol loss from the fermenting liquid phase (g/L, % vol/vol, or % wt/wt) during an entire batch fermentation is proportional to the square of the concentration of sugar utilized. If ethanol loss is expressed as a percentage of ethanol formation, then this quantity is directly propor-

tional to the concentration of sugar utilization.

This effect is dramatically demonstrated by the computer model results shown in Figure 5. A series of fermentations at 21.1°C with initial sugar contents ranging from 10°Brix to 30°Brix were simulated. Sugar and ethanol inhibition effects on yeast growth were suppressed in this run, allowing simulation of complete sugar

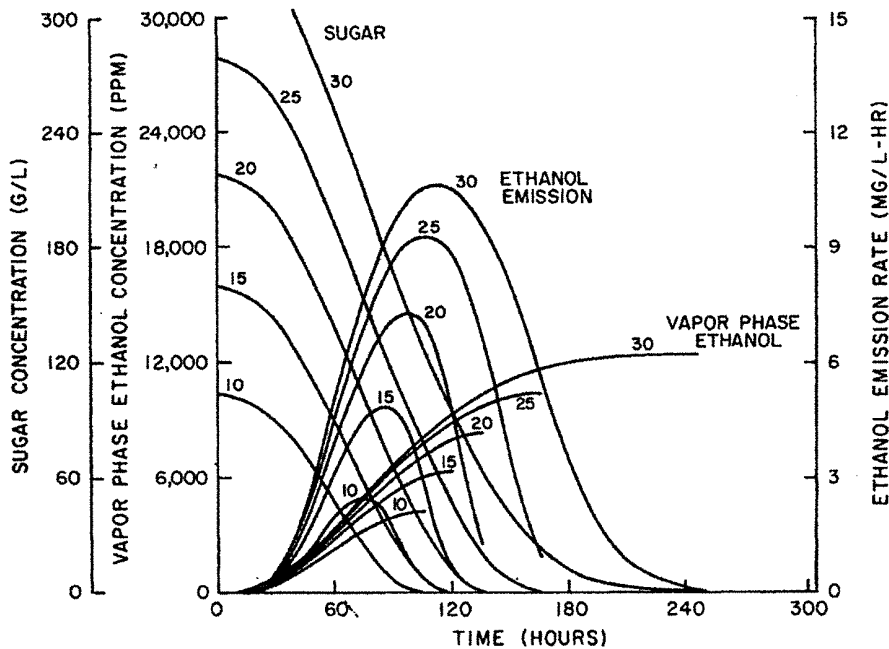


Fig. 5. The influence of initial sugar content on the rate of fermentation, the rate of ethanol emission and the vapor phase ethanol concentration. (Isothermal T=21.1°C.)

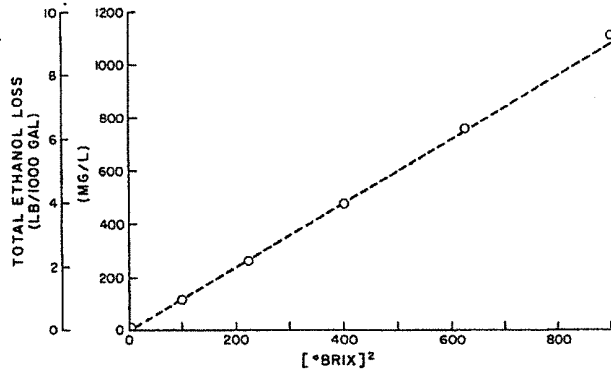
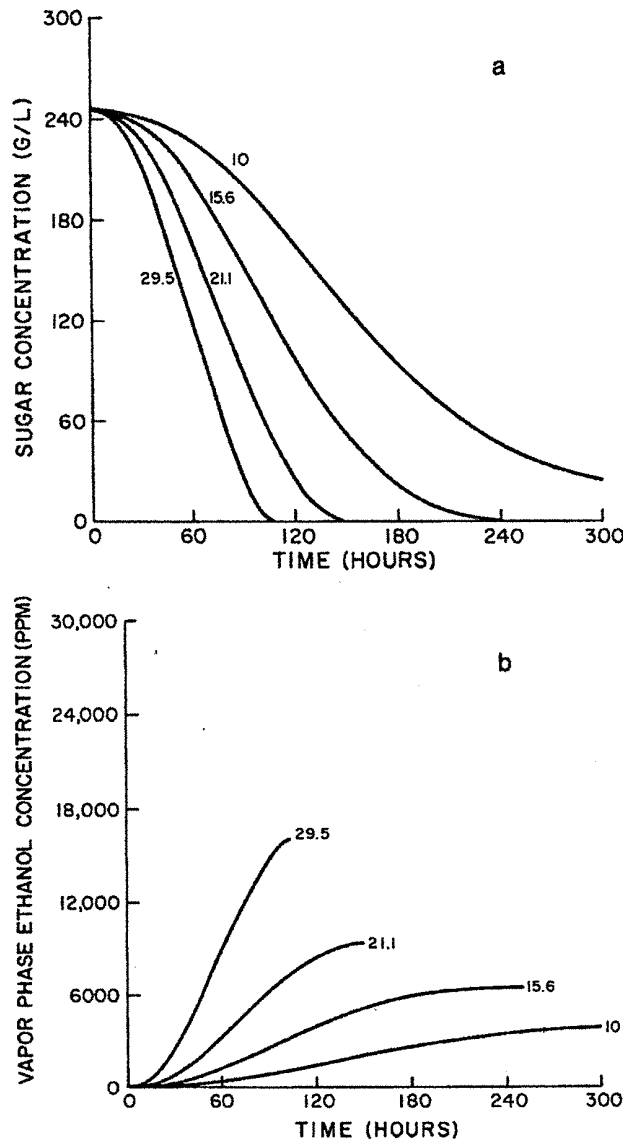


Fig. 6. The relationship between the square of the sugar content utilized during a fermentation and the total ethanol lost. (Data from Figure 5.)



utilization of even the high sugar values. It can be seen that the final vapor phase ethanol concentration increases more or less proportionally with sugar utilization. However, the area under the ethanol loss rate curves increases much more dramatically. Comparison of the 30°Brix curve with the 10°Brix curve shows a loss much larger than three times as great, in fact, more in the range of nine times as great. A plot of the computer generated values of total loss against the square of the °Brix utilized (Fig. 6) results in almost a straight line, verifying the previously derived theoretical relationship (17). The minor deviation from linearity is the result of assumptions built into the model. It should be emphasized that the results in Figure 6 only apply to entire fermentations of juice at 21.1°C. Other temperatures would produce lines with different slopes.

Effects of fermentation temperature: As previously discussed, the effects of temperature on fermentation rate *per se* have no bearing on ethanol evaporative loss. The overwhelming effect of temperature is on the partial pressure exerted by ethanol from aqueous solutions. Two separate temperature dependencies are involved; that of the pure component vapor pressure, as described by the Antoine equation, and that of the ethanol activity coefficient, as described by solution thermodynamic relationships. It has been shown (17) that both of these dependencies can be approximated in the region of

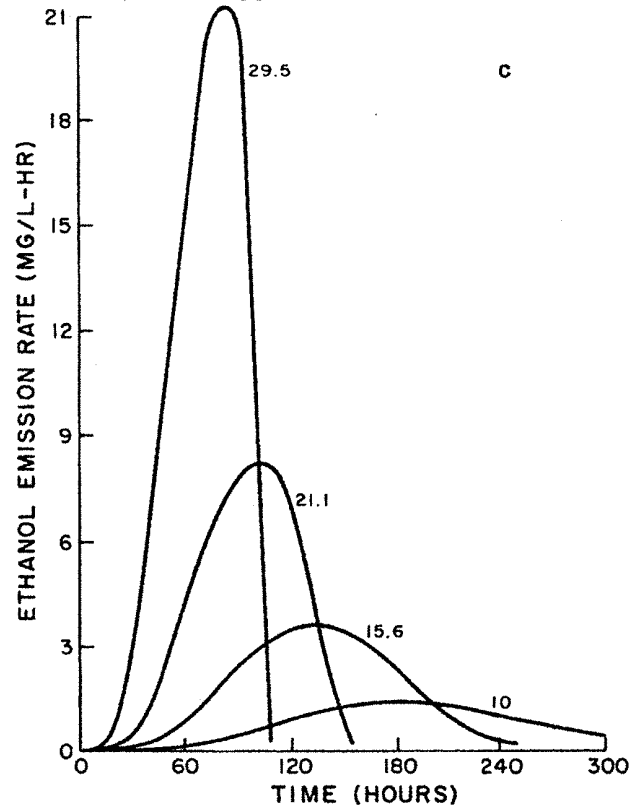


Fig. 7. The influence of fermentation temperature on a) the fermentation rate, b) the vapor phase ethanol concentration, and c) the rate of ethanol emission. (Initial sugar content of 22.5°Brix, isothermal fermentation at indicated temperature.)

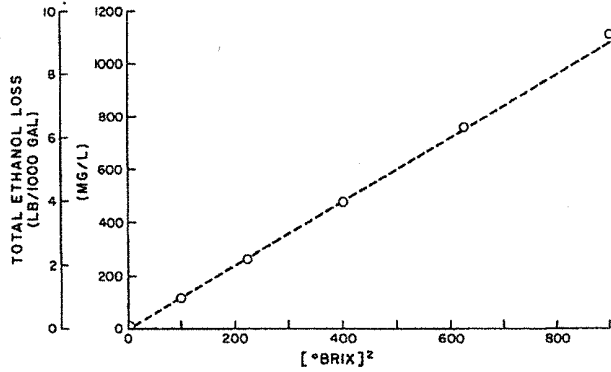
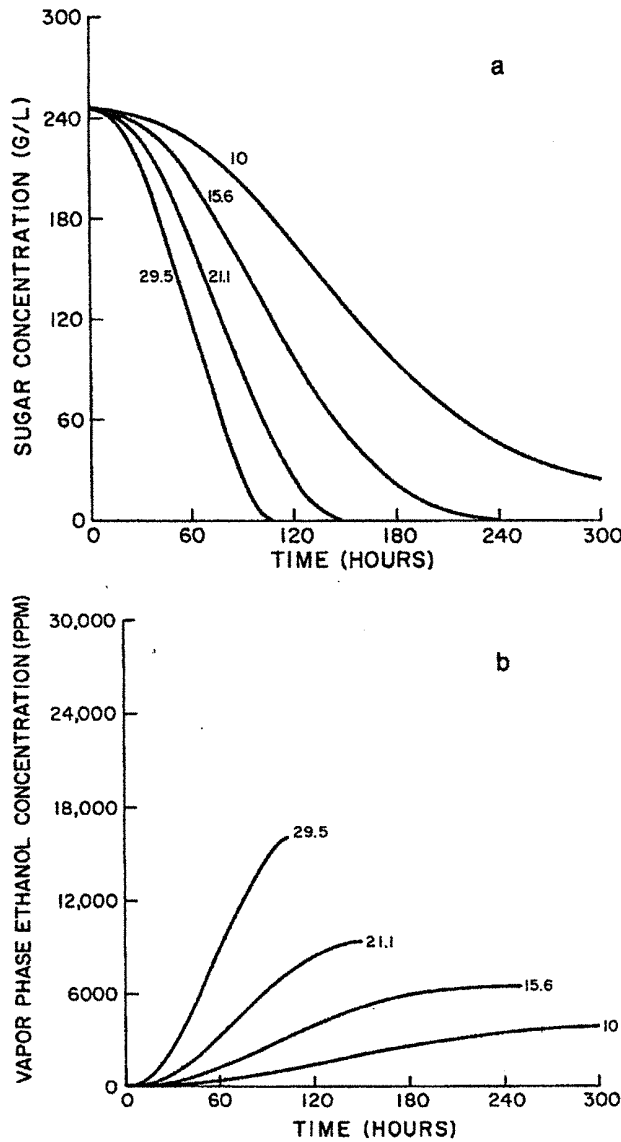


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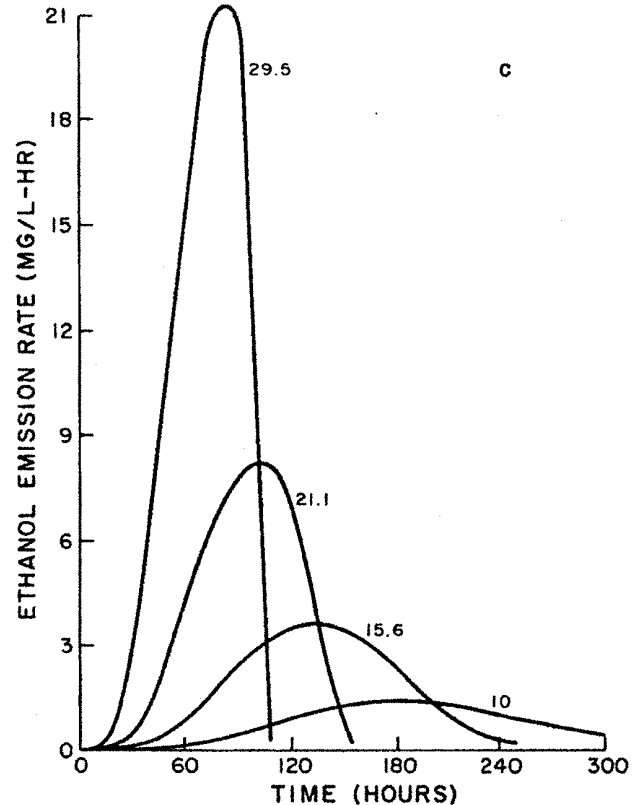


Fig. 7. The influence of fermentation temperature on a) the fermentation rate, b) the vapor phase ethanol concentration, and c) the rate of ethanol emission. (Initial sugar content of 22.5°Brix, isothermal fermentation at indicated temperature.)

fermentation interest, 0-40°C, by a single term whose logarithm is inversely proportional to absolute temperature. With other conditions constant, a plot of the logarithm of ethanol loss against the reciprocal absolute temperature will yield a straight line.

A series of isothermal fermentations, all at 22.5°Brix was simulated for temperatures ranging from 10°C up to 29.5°C. The resulting curves, shown in Figures 7a, 7b, 7c, follow the expected trend regarding fermentation rates. However, the important point to note is the large increase of vapor phase ethanol concentration with temperature, going from about 4000 ppm at 10°C to over 16 000 ppm at 29.5°C. Likewise, the total ethanol loss went from 280 mg/L to 1064 mg/L, corresponding to 2.34 and 8.85 lb/1000 gallons, respectively.

As shown in Figure 8, the losses predicted by the computer simulation for 22.5°Brix sugar utilization indeed fall in a straight line on a semi-log plot against reciprocal absolute temperature. At other values of °Brix, the respective lines would be parallel and either higher or lower as indicated.

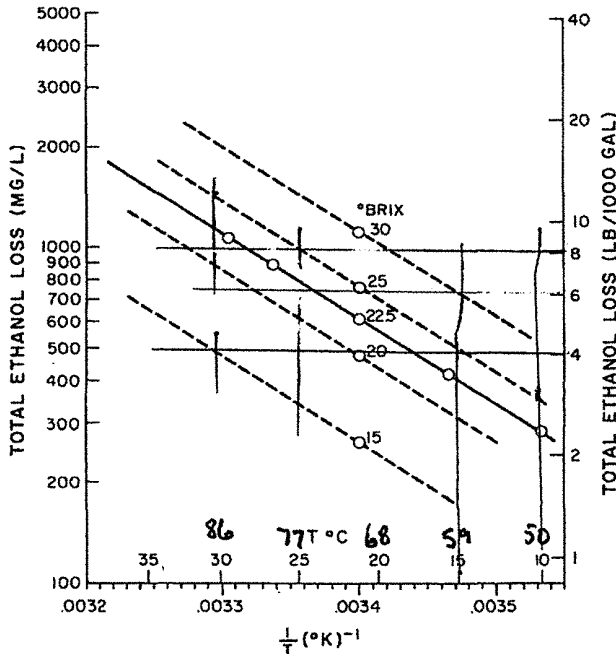


Fig. 8. The linear relationship between the reciprocal absolute temperature and the logarithm of the total ethanol lost for the initial sugar contents indicated.

Effect of sugar and temperature: In fact, it is possible to simultaneously correlate both the effects of temperature and sugar concentration utilized, resulting in a single linear correlation for all isothermal entire fermentations (17). It is merely necessary to plot the quantity

$$\log \frac{\text{Ethanol lost}}{[\text{Sugar concentration used}]^2}$$

against reciprocal absolute temperature, and all of the parallel lines in Figure 8 should collapse into a single

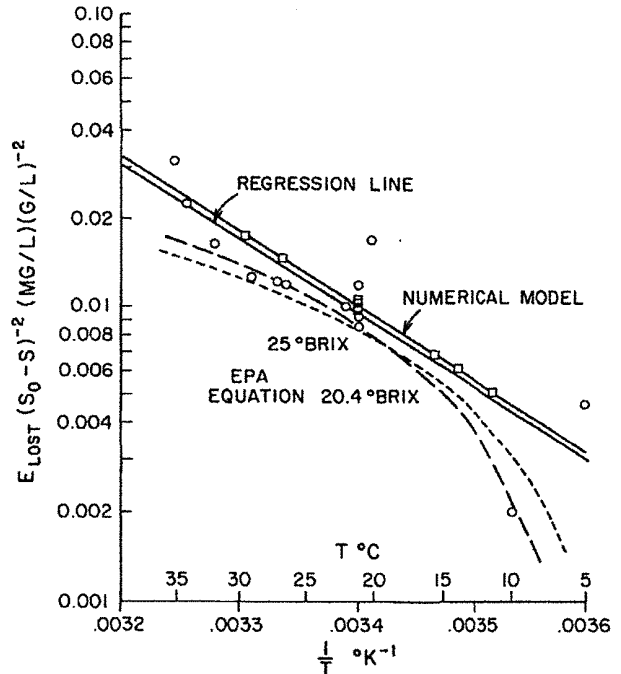


Fig. 9. The general linear relationship between the reciprocal absolute temperature and the logarithm of the ethanol lost divided by the square of the sugar concentration utilized. Model predictions (O), EPA equation (15) for 20.4°Brix (---) and 25°Brix (---).

straight line. This plot is shown in Figure 9, which contains points from several isothermal fermentation simulation cases and also the reported literature values based on the information in Table 1.

It may be seen that the computer simulation points all fall on a straight line. The dispersed cluster of calculated points at 21.1°C corresponds to isothermal cases with sugar utilization ranging from 10°Brix to 30°Brix. Thus, all of the parallel lines in Figure 8 did not collapse exactly into a single line on this plot. This is due to some assumptions made in the computer model and the theory behind this form of plot. However, the predicted loss values come very close to one another, even over such a wide range of sugar utilization values.

The regression line through 13 reported literature data points from Table 1, is almost parallel to and slightly below the predicted values. Data points which only pertained to partial fermentations were excluded, as was the one report on a grain fermentation (6), which seems to be in error by at least an order of magnitude.

Also shown in Figure 9 are curves generated by a recently published EPA prediction equation (15), which has no theoretical basis. This equation deviates from linearity on a plot such as Figure 9 and generally underestimates ethanol losses, especially at lower temperatures.

The best available estimates for ethanol evaporative losses during entire, isothermal juice fermentations at any combination of sugar utilization and temperature should be obtainable from the computer line in Figure 9.

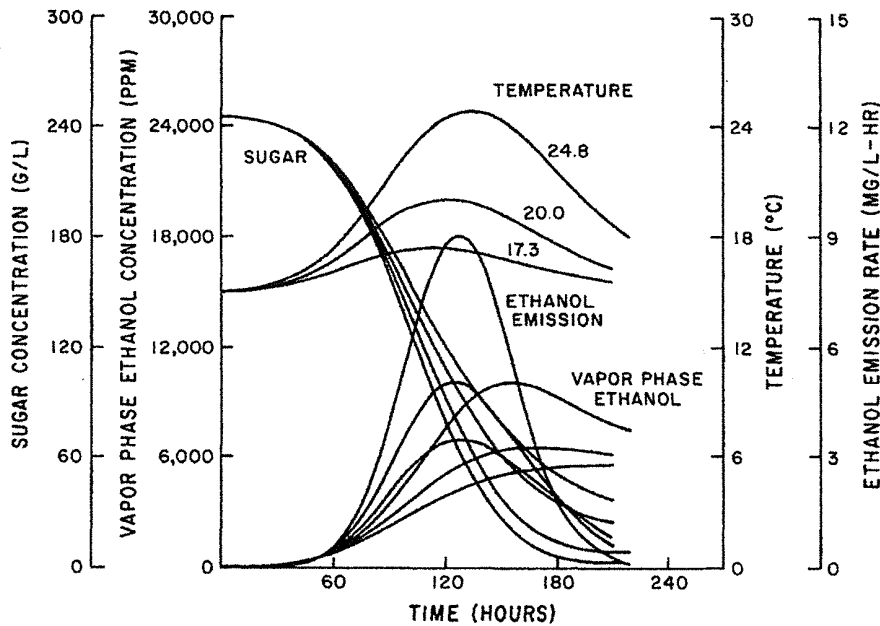


Fig. 10. The influence of non-isothermal fermentation on the rate of ethanol emission and the vapor phase ethanol concentration. (Initial sugar content of 22.5°Brix, initial temperature of 15°C maximum fermentation temperature as indicated.)

Non-isothermal cases: It sometimes happens in fermentation practice that the capacity of cooling systems in not sufficient to maintain fermentations at constant temperatures. The versatility of this modeling approach is that it is also capable of describing behavior in these complex non-isothermal cases. Figure 10 shows the result for a series of 22.5°Brix fermentations, initially at 15°C, which reached peak temperatures of 17.3°C, 20.0°C and 24.8°C due to varying deficiencies in cooling capacity. It can be seen that this condition results in a skewing of the ethanol emission rate curves toward later times. In addition, the vapor phase ethanol concentration often peaks during fermentation rather than at the end. Figure 11 shows the corresponding result of fermenta-

tions initially at 20°C which reached temperatures of 21.6°C, 23.3°C and 26.8°C. The ethanol emission rates

Table 2. Effect of non-isothermal fermentation.

Percent of maximum cooling load	Temperature °C Initial	Temperature °C Maximum	Maximum vapor ethanol ppm	Total ethanol loss g/L	Lb/1000 gal
100	15	15	5330	0.310	2.59
50	15	17.3	5512	0.346	2.88
25	15	20.0	6454	0.437	3.65
12.5	15	24.8	10037	0.656	5.48
100	20	20	8395	0.531	4.43
50	20	21.6	8516	0.585	4.88
25	20	23.3	8943	0.659	5.50
12.5	20	26.8	11607	0.829	6.92

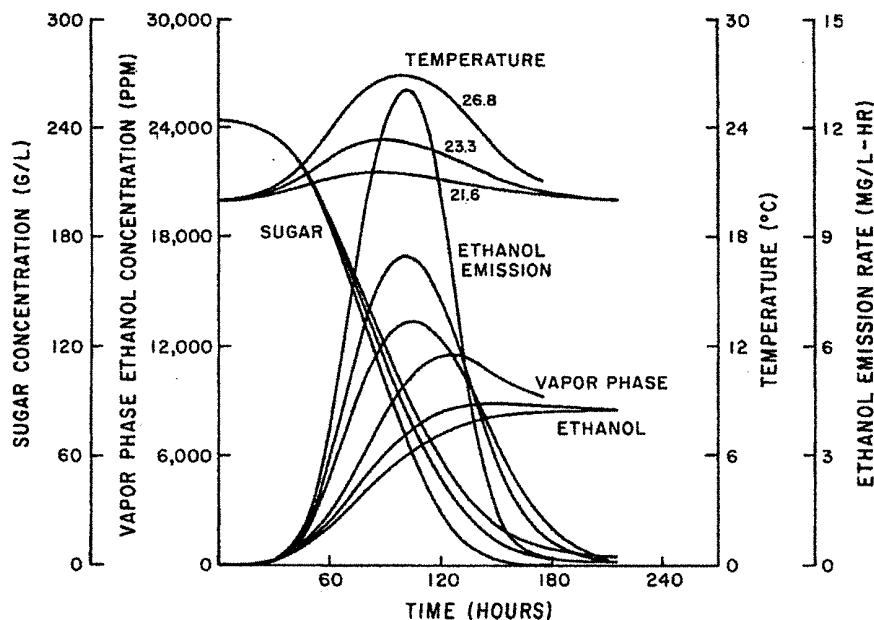


Fig. 11. The influence of non-isothermal fermentation on the rate of ethanol emission and the vapor phase ethanol concentration. (Initial sugar content of 22.5°Brix, initial temperature of 20°C, maximum fermentation temperature as indicated.)

are higher due to the higher peak temperatures. The maximum vapor phase ethanol concentration can again reach a maximum before the end of fermentation providing the temperature rise is of the order of 5°C. The total losses also increased greatly, as shown in Table 2.

Effect of cap: All of the previous simulations have been for cases of batch juice fermentations which assumed homogeneity throughout the fermenting liquid. The presence of a partially submerged cap of grape skins in red wine fermentations is known to introduce rather large inhomogeneities in both temperature and the concentrations of sugar and ethanol. Guymon and Crowell (9) observed temperatures in caps as much as 8° to 11°C higher than the liquid temperature. This was attributed to a more rapid rate of fermentation associated with a much larger accumulation of yeast cells mass adhering to the skin surfaces in the cap. They also found that the liquid pressed from the cap had a higher alcohol concentration and lower reducing sugar concentration than the bulk liquid, but the degree of disparity varied throughout the batch. Clearly, the phenomena occurring in the cap are complex and would require a much better knowledge of the cap microstructure before an accurate model could be developed.

However, a simplified simulation model, which probably underestimates ethanol losses, can be developed and examined. It is assumed that the cap is wetted with liquid at the same ethanol concentration as the bulk liquid, but is at a higher temperature, ranging from 0° to 10°C higher than the bulk liquid. Thus, fermentation proceeds at the

bulk liquid temperature, but ethanol vapor equilibrium concentrations are calculated at the higher cap temperature.

The results of this simulation for 22.5°Brix sugar utilization are shown in Figure 12. It can be seen that increasing liquid-cap temperature differentials significantly increase vapor phase ethanol concentrations and total ethanol loss. The numerical results are summarized in Table 3.

Table 3. Effect of cap temperature $T_{\text{Bulk}} = 21.1^\circ\text{C}$

Cap ΔT °C	Vapor ethanol ppm	Ethanol loss	
		g/L	Lb/1000 gal
0	9325	0.61	5.09
2.5	11019	0.72	6.01
5.0	12980	0.85	7.09
7.5	15242	1.01	8.43
10.0	17844	1.18	9.85

Because of the fact that liquid present in the cap may contain ethanol concentrations twice as large as the bulk liquid (9), the results in Table 3 could be low by at least 50%. On the other hand, if the CO₂ passing through the cap does not attain equilibrium with the cap temperature and ethanol concentrations, then the values in Table 3 could be too large.

Clearly, if reduction of evaporative ethanol loss is one goal for fermentation management, then more intensive cap management by pumping over or other means will minimize temperature differentials, and advancing the time for cap removal would significantly reduce evaporative ethanol emissions.

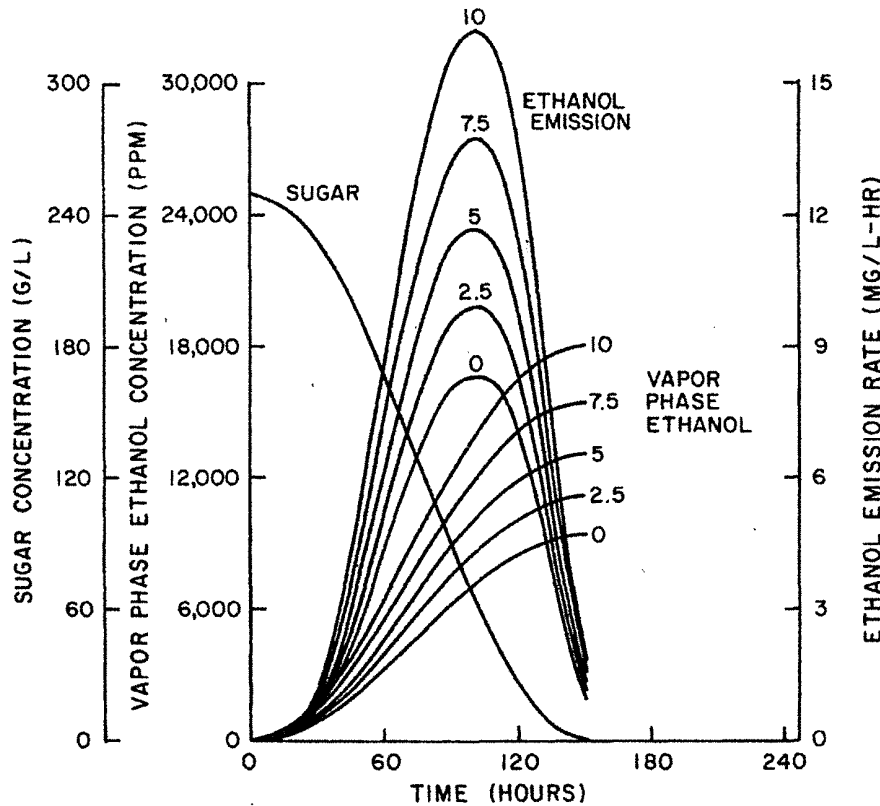


Fig. 12. The influence of elevated skin cap temperature on the rate of ethanol emission and the vapor phase ethanol concentration. (Initial sugar content of 22.5°Brix, liquid temperature of 21.1°C, temperature differentials as indicated.)

Conclusions

A batch alcoholic fermentation model has been developed and demonstrated to accurately predict expected losses of ethanol due to evaporation. Agreement with experimental results is good, with the model probably being more accurate than the experimental measurements available.

Fermentation rate *per se* has no effect on amount of ethanol loss. The concentration of sugar utilized has a strong effect, with the loss proportional to the square of the concentration utilized. Temperature also has very important effects as manifested in the results for non-isothermal simulations and for isothermal simulations at various temperature differentials in the presence of a skin cap.

The prediction of ethanol evaporative loss is much more complex than previous treatments have indicated. The use of single value emission factors or of empirical regression equations with no theoretical basis will generally not result in a correct value for ethanol loss. The only reliable approach involves application of theory and mathematical modeling supported by reliable physical property data to the given situation. The master correlation plot presented here, which includes the effects of both temperature and sugar concentration utilized, constitutes the best available method for estimating ethanol evaporative loss in wine fermentations.

Literature Cited

1. Amerine, M. A., and M. A. Joslyn. *Table Wines — The Technology of Their Production*. 2nd ed. p. 350. Univ. California Press, Berkeley (1970).
2. Amerine, M. A., and C. S. Ough. *Methods for Analysis of Musts and Wines*. p. 77. John Wiley, New York (1980).
3. Boulton, R. Kinetic model for the control of wine fermentations. *Biotechnol. Bioeng. Symp.* No. 9:167-77 (1979).
4. Boulton, R. The prediction of fermentation behavior by a kinetic model. *Am. J. Enol. Vitic.* 31:40-5 (1980).
5. Bremond, F., and J. Roubert. Récupération de l'alcool entraîné par le gaz carbonique des fermentations viniques. *Vignes et Vins* 14:22-8 (1951).
6. Carter, R. V., and B. Linsky. Gaseous emissions from whiskey fermentation units. *Atmos. Environ.* 8:57-62 (1974).
7. Flanzly, M., and V. Boudet. Les pertes d'alcool au cours de la transformation des jus de raisin en vin. *Viticult. Arboricult.* 95:104-7 (1949).
8. Gay-Lussac, J. Observations sur cette question: Quelle est la quantité d'alcool qui est entraîné par l'acid carbonique, pendant la fermentation du moût de raisin?. *Ann. de Chim. et de Phys. Ser. 2* 18:380-9 (1821).
9. Guymon, J. F., and E. A. Crowell. The nature and cause of cap-liquid temperature differences during wine fermentation. *Am. J. Enol. Vitic.* 28:74-8 (1977).
10. Nègre, E. Levurage et remontages. VII. Aérations et pertes d'alcool. *Le Progress Agric. et Vitic.* 126:238-42 (1946).
11. Ouchida, P. Evaluation test to measure ethanol emissions from a 106,000 gallon fermentation tank. Engineering Evaluation Branch Report No. C-80-071, California Air Resources Board, Sacramento (1980).
12. Ough, C. S., and M. A. Amerine. Effects of temperature on wine making. *Bull. Calif. Agric. Expt. Sta.* 827, p. 16 (1966).
13. Pemberton, R. C., and C. J. Mash. Thermodynamic properties of aqueous non-electrolyte mixtures. II. Vapour pressures and excess Gibbs energies for water + ethanol at 303.15 to 363.15 K determined by an accurate static method. *J. Chem. Thermodynamics* 10:867-88 (1978).
14. Saller, W. Die Qualitätsverbesserung der Weine und Süsse durch Kälte. p. 73. Verlag Sigurd Horn, Frankfurt/Main (1955).
15. U. S. Environmental Protection Agency, Supplement No. 10 for Compilation of Air Pollutant Emission Factors-AP42, Section 6.5.2 (Feb. 1980).
16. Warkentin, H., and M. S. Nury. Alcohol losses during fermentation of grape juice in closed fermenters. *Am. J. Enol. Vitic.* 14:68-74 (1963).
17. Williams, L. A. Theory and modeling of ethanol evaporative losses during batch alcoholic fermentation. *Biotechnol. Bioeng.* 25:1597-612 (1983).
18. Zimmerman, H. W., E. A. Rossi, Jr., and E. Wick. Alcohol losses from entrainment in carbon dioxide evolved during fermentation. *Am. J. Enol. Vitic.* 15:63-8 (1964).