CREATING A DISCRETE MODEL OF SAP PROCESSING THERMODYNAMICS

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Introduction

Running a successful maple syrup operation requires attention to detail, specifically with regards to production efficiency. Despite new technology and the innovation of new production methods, the amount of energy it takes to bring sap to the sugar concentration (measured as degrees Brix or °Bx) for maple syrup remains constant. The rule of thumb used to help sugar makers estimate their fuel costs was that it takes 400,000 BTU to bring 2 °Bx sap into maple syrup.[1] This rule of thumb is a close estimate, but it neglects the change in boiling point as the solution becomes more concentrated. Additionally, the amount of energy required to boil changes depending on the final concentration of syrup.[2] The thermodynamic model of the sap boiling process presented here accounts for changes in the composition of the solution as it undergoes boiling, resulting in a difference in energy of +5%, +3%, and +1% for 68, 67, and 66 °Bx syrup respectively. These differences are important for all sugar makers, as they also directly affect the cost of fuel per gallon of syrup for all fuel types. This model can be used by sugarmakers when calculating how much fuel they would need at different levels of concentration and with different fuel types to assess costs associated with producing maple syrup.

Thermodynamic Model

Sap is composed mainly of sucrose and water.[3] The remaining solids represent a negligible fraction of the composition of sap when it comes out of the tree, allowing sap to be treated as an ideal solution of sugar and water. In a standard season across the maple producing geographies of North America, the average initial sugar content of sap leaving the tree is 2 °Bx. From Sokolovsky (1958, p. 19),[4] the empirical approximation of the boiling point of sucrose-water solutions is:

$$T(°C) = 100 \ °C + 2.33(S \ / \ W) \qquad \text{(eqn. 1)}$$

where S is the concentration of sucrose in solution and W is the concentration of water. For high concentrations of sucrose, like we see in syrup, the boiling point approaches 105 °C.[5] As the composition of the solution changes with concentration, so does the specific heat capacity, which is directly proportional to mass:

$$Cp = (m \ \Delta T) \ / \ Q \qquad \text{(eqn. 2)}$$

This relationship was quantified empirically by Sokolovsky (1958, p.32):[4]

$$Cp = 1 - (0.6 - 0.0018t)S \qquad \text{(eqn. 3)}$$

2

where *t* is the temperature of the solution (in this case the boiling point) for any given concentration S.

The energy supplied to the system to bring it to a boil and have the water evaporate into steam (therefore increasing the overall concentration of sugar in the solution) can be broken into two physical properties of the system: Q_{boil} and $Q_{vaporization}$. The first energy, Q_{boil}, was encountered above in the relation of specific heat capacity and represents the amount of energy needed to bring the solution to its boiling point from some initial temperature (ΔT) based on the amount of solution being heated (m) and the bulk physical properties of the solution that allow for the transfer of heat and subsequent increase in temperature (C_p). The second energy is the internal energy of the system that allows for a phase change:

$$Q_{vaporization}=mL_v=mH_v$$

where L_v is the latent heat of vaporization.[6] L_v is a physical property (also known as the enthalpy of vaporization H_v) that is essentially the energy needed to overcome the internal molecular forces constraining the kinetic degrees of freedom from one phase of matter to another.[7] Because the pressure tends to remain constant at the instant of a liquid-gas phase change, the change in the Gibbs' free energy ΔG is zero, meaning there is no pressure-volume work done through boiling the sucrose-water solution (an isobaric process) and is in equilibrium at that instant.[8]

$$\Delta G = \Delta H - T\Delta S = 0, \quad \Delta H = T\Delta S = TdS \quad \text{(eqn. 4)}$$

Substituting this case into Maxwell's thermodynamic relations we can see that enthalpy H is directly related to energy:[7]

$$dU = TdS - PdV = dH - PdV \quad \text{(eqn. 5)}$$

$$\Delta H_v = \Sigma(\Delta U + P\Delta V) = \frac{Q_{vaporization}}{m} \quad \text{(eqn. 6)}$$

where U is the internal energy of some amount of the system (energy per unit mass), P is the pressure, and V is the volume. Thus, allowing us to see what properties of the solution *(U, P, V)* make up $Q_{vaporization}$ for the bulk system.

Calculating the enthalpy of vaporization requires that one knows the pressure of the solution as it undergoes a phase change, also known as the vapor pressure.[9] As stated above, sugar-water solutions are considered ideal solutions. They are ideal because sucrose completely dissolves in water, meaning that the forces between the sucrose and the water are equal to the forces between the water molecules themselves, allowing for the same amount of energy to be needed to evaporate water from the surface during a phase change as if it was purely water.[9,10] Additionally, the activity of sucrose is equal to the concentration in an ideal solution, meaning

the sucrose-sucrose interactions are negligible in solution. Sucrose is a non-volatile compound, meaning that it does not vaporize easily due to strong intramolecular forces.[11] It is important to note that the non-volatility of sucrose and the ideal nature of the solution is what was used in the rule of thumb for total energy needed to boil sap into a gallon of syrup. Due to these properties, the vapor pressures of different concentrations of sap and syrup can be calculated using Raoult's Law:[10,12,13]

$$P_{solution} = X_{solvent} \, P_{solvent} \quad \text{(eqn. 7)}$$

where $X_{solvent}$ is the molar fraction of water in the sap. For water, the pressure of vaporization above 100 °C is non-linear and can be approximated as a function of temperature (in °C):[14]

$$P_{solvent} = 2427.9 - 60.726 \, T + 0.44048 \, T^2 \quad \text{(eqn. 8)}$$

This approximation becomes necessary as the boiling point increases past the boiling point of pure water. As you can see from the relation above, the vapor pressure of the solution $P_{solution}$ continues to decrease as the sugar concentration of the solution increases as it is directly proportional to the decreasing molar fraction of water in the solution.

Using the vapor pressure and boiling point as the pressure and temperature constants at the point of phase change, one can use the Clausius-Clapeyron relation (eqn. 9) to determine the enthalpy of vaporization (H_v, in units of Joules per mol (J/mol)):[7,15,16]

$$ln \, (P_1 \, /P_2 \,) = (-\Delta H_v \, / R)(1/T_1 \, - \, 1/T_2 \,) \quad \text{(eqn. 9)}$$

where P_1 is the vapor pressure of sap at initial temperature T_1 = 40 °F (4.44 °C), and P_2 is the vapor pressure at the boiling point (T_2) calculated at each concentration of sucrose. To obtain enthalpy of vaporization in units of Joules per kilogram, the weighted molality of the solution at each concentration is multiplied by the enthalpy of vaporization found in eqn. 9. The weighted molality is calculated by multiplying the molar fraction of each part of the solution times its respective molality to get mass (m).

We now have our change in enthalpy of vaporization based on known physical properties of the system--concentration (°Bx), which is used to determine partial pressure, and temperature (°C). We can now use the change in enthalpy to create a discrete sum as the solution increases in concentration (one °Bx at a time). However, we also need to know how much mass is being lost as it boils and becomes more concentrated. We now need to figure out how many gallons of sap are needed to produce one gallon of finished syrup.

Modified Jones Rule of 86

Each physical property (enthalpy (H_v), vapor pressures (P_1 and P_2), boiling temperature (T_2), and sucrose concentration (X)) was calculated on a discrete basis between 2 and 68 °Bx with a ΔX of 1 °Bx. To accurately estimate the amount of energy required to boil, one must also consider the change in mass of the solution as water is evaporated. The other major rule of thumb in the sugar making community is the Jones Rule of 86, based on the 1946 paper by C.H. Jones, which approximated the amount of sap necessary to create one gallon of 65.5 °Bx syrup based on the starting Brix of sap. This rule was to take the number 86 and divide it by the starting Brix to obtain gallons of sap.[2,17] However, as recent modifications to the rule have pointed out, syrup can be anywhere from 66 to 68.9 °Bx to be considered legal.[18]

To reconcile this, a physical rule was derived for the loss of mass as sap undergoes boiling. Because sucrose is a non-volatile compound, the amount of sucrose (in terms of mass) stays constant while the amount of water decreases, which leads to the concentration increase. Knowing this, one can take the density of finished syrup (~1333 kg/m³ or ~5 kg/gal at 68 °Bx) and multiply it by the percent sugar content of the syrup (°Bx/100) to find out the mass of sugar in one gallon of syrup. Because this number remains constant through boiling, the initial amount of sap needed can be calculated as the mass of sucrose divided by the density of the sap coming out of the tree. This results in a final relationship:

$$\# \; Gallons \; sap \; per \; Gallon \; Syrup = \frac{(X_f \, m_f)}{(X_i \, \rho_i)} \qquad \text{(eqn. 10)}$$

where m_f is the density of finished syrup times one gallon, X_f and X_i are the final and initial concentrations of sucrose in solution respectively, and ρ_i is the density of amorphous sucrose, allowing for the dimensionless relationship:

$$\# \; Gallons \; sap \; per \; Gallon \; Syrup = \frac{(X_f \, \rho_f)}{(X_i \, \rho_i)} \qquad \text{(eqn. 11)}$$

to yield the same result. As most sugarmakers use a hydrometer regularly to check the density of their syrup, one can always know how many gallons of sap they would need at any combination of input and output °Bx. It should be noted that the density of sugar solutions do not vary linearly with concentration as one would expect, because as sucrose crystallizes from its original amorphous form, its density changes with its physical structure. Using the starting and ending states that sucrose ends up in solution, we can approximate this linearly based on the range of densities (1507.7 kg/m³ – 1586.2 kg/m³). Empirically, eqn. 11 can be rewritten using only starting and ending °Bx concentrations:

$$\# \; Gallons \; sap \; per \; Gallon \; Syrup = \frac{(-3.384)*10^{-3}*X_i*X_f+1.017 \, X_f}{(-3.714)*10^{-3}*X_i*X_f+1.017 \, X_f} \qquad \text{(eqn. 12)}$$

Using this ratio on a discrete basis allows for an accurate calculation of the decrease in water weight as you boil down 1 °Bx at a time. Using physcial properties of water and sucrose,[11,19–24] the mass of solution that remains after it is concentrated on a °Bx by °Bx basis was calculated to determine the energy needed to bring it to its next boiling point Q_{boil} and the energy expended in vaporizing that mass of water $Q_{vaporization}$.

$$Q_{boil} = \sum_{Ti}^{Tf} m\, Cp\, \Delta T \qquad \text{(eqn. 13)}$$

$$Q_{vaporization} = \sum_{mi}^{mf} \Delta m\, Hv \qquad \text{(eqn. 14)}$$

Adding these discrete sums together yields the total energy of the system. For 2→68 °Bx syrup this is 436,196 BTUs, 2→67 °Bx syrup this is 427,730 BTUs, and for 2→66 °Bx syrup this is 419,333 BTUs.

Evaporators and Thermal Efficiency

Quantifying the amount of energy needed to boil sap is the first step towards reducing emissions and lowering fuel costs. The second step is identifying the different types of evaporators, along with their corresponding fuels and efficiencies. The two most used types of evaporators are wood-fired arches and oil-fired evaporators. Wood-fired arches are designed to burn solid fuels (including coal, pellets, and wood chips) and to direct air movement from the firebox out through the flues and up the stack. The constant flow of heat from the firebox to the flue and the combustion of gasses along the length of the pan allows for consistent heating across the entire surface.[25] Efficiencies of wood fired evaporators range from 35-50% depending on insulation of the arch and pans as well as adequate air flow.[26] Beyond proper insulation techniques, one can improve heat transfer through forced draft. The forced draft blower increases the amount of oxygen supplied to the fire box, pressure builds and leads to an increase in both heat transfer and turbulence.[27] The increase in turbulence is due to a jet of air moving at a higher velocity than the surrounding air of the fire box, along with sharp edged grates to agitate airflow. Increasing turbulence reduces the insulation effect of the fluid boundary layer along the surface of the pans, increasing heat transfer to the metal. One can expect an increase in energy transfer of about 10-20% with the use of forced draft.[28]

Oil fired evaporators are more efficient than their wood fired counterparts with an efficiency of 73-80%, with newer models being closer to 80%.[28,29] They work by atomizing liquid fuels and creating radiant heat below the pans for efficient heat transfer.[25] Enhancements in efficiency have been researched through the addition of steam hoods and preheaters, which are more commonly associated with oil fired evaporators, but can be used with any arch if they are sized properly. Preheaters work like a condensing boiler, capturing the energy of the water vapor that is evaporated off the syrup and condensing it instead of losing it to the environment.[29] This

energy is used to heat up incoming cold sap, greatly reducing the amount of energy needed to bring it to a boil. This process is performed with the help of a hood over the pan to lock in water vapor. Some units also use dry air to agitate sap and release water under the temperature of boiling, increasing the sugar concentration without expending extra heat.[28] The use of a preheater can increase efficiency by 15-20%.[28–30] Full steam enhanced units (Steam-Away™ produced by Leader Evaporator) have been rated by the manufacturer to increase evaporator rates by 65-75%.[31] Thermodynamically, we expect about a 16% decrease in overall energy consumption when sap is heated to just below the boiling point using ambient steam (see Figure 1).
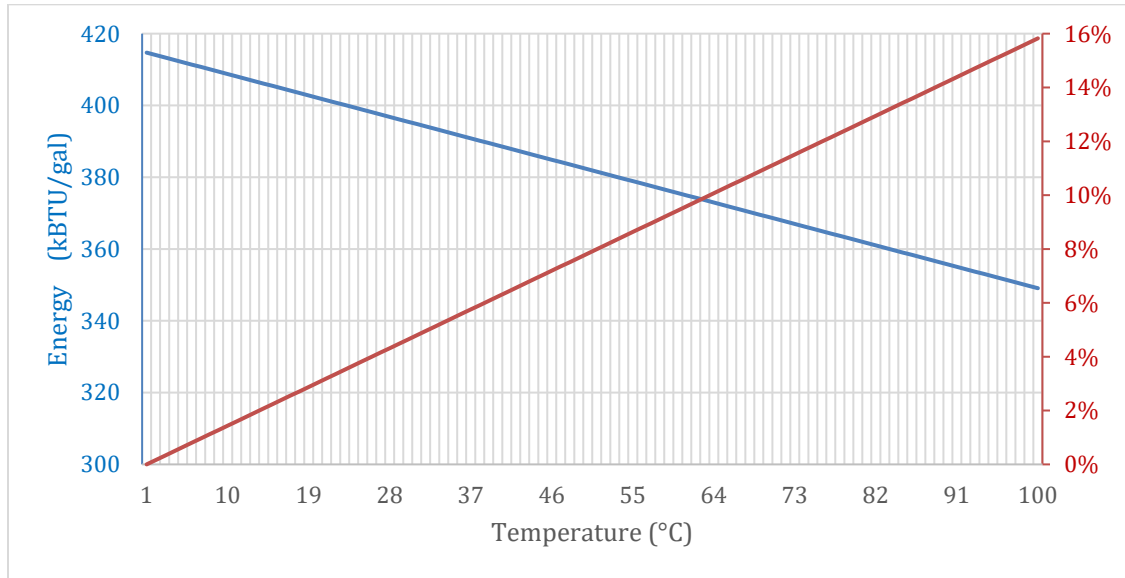
Figure 1 Remaining energy to make one gallon of finished syrup at 67 °Bx at different initial temperatures. The right axis represents the efficiency increase in terms of the total energy saved per gallon of finished syrup.

Additionally, flue pans with increased surface area can allow for enhanced heat transfer, raising the efficiency of any type of evaporator. Less common evaporator types would include those that burn natural gas and propane, or fully electric models. Natural gas and propane evaporators work similarly to the oil and wood fired arches mentioned above, but not much research has been done on their efficiency.[32] Because a propane or natural gas unit relies on the combustion of gas and the flow of air, it is expected to have a similar efficiency to that of a forced draft wood evaporator at around 65%-70%, consistent with studies of older gas based evaporators.[29,30,33] Electric units work by preheating sap and using a steam generator to create heat. The steam increases the pressure and temperature of the sap, and energy from condensate is captured and reused.[34] It is assumed that electric evaporators have an efficiency upwards of 90% and are most likely close to 100% as the units obey the same physical principles as electric resistance heating.[35]

Concentration

Another way to reduce fuel consumption is through the concentration of sap to a higher °Bx through reverse osmosis (RO) before boiling.[36,37] RO works by creating a pressure gradient either through a pump or a vacuum and running fluid through a micro or nano-filter membrane.[38] Normally, RO is used for the desalination or purification of water, where the permeate is the product and the concentrate is the waste. For producing higher concentrations of sugar, the concentrate is the desired product, and the permeate is the waste.

The energy necessary to produce finished syrup decreases hyperbolically as the input sugar concentration increases. Figure 2 is a direct illustration of the efficiency increases in boiling with concentration, meaning it does not factor in RO performance, energy, or the heat the RO unit applies to the sap. It should be noted that there is a loss of RO efficiency with colder input sap (75% at 40 °F), and the slight pre heating effect you get by running sap through the membrane (40 °F to 55 °F).[39] The act of bringing sap from just 2 °Bx to 4 °Bx results in fuel savings of 54.5%, while bringing sap to a high input concentration of 20 °Bx results in fuel savings of 94% (see Figure 2).
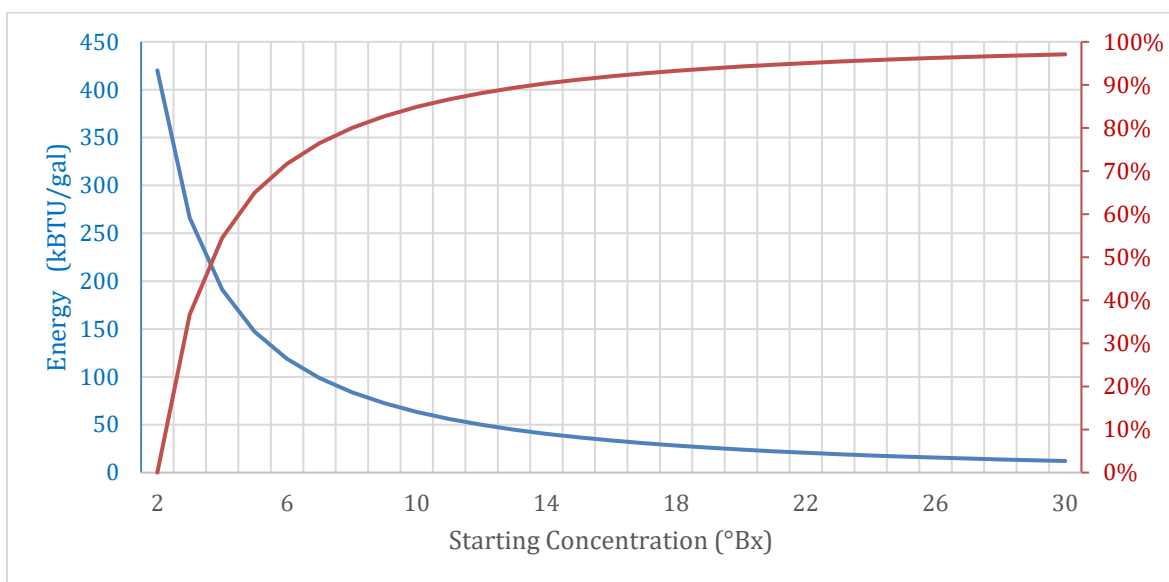

Figure 2 Remaining energy to boil sap into finished syrup (67 °Bx) and efficiency changes based on different starting concentrations.

While reverse osmosis has been rumored to change the flavor profile of syrup, research has shown that there is no significant change in the composition or flavor of syrup concentrated up to at least 21.5 °Bx.[40] The other major deterrent is the high upfront capital cost of an RO unit. However, as fossil fuels (like No. 2 fuel oil) continue to become more expensive, the payback period for an RO unit continues to decrease.

The question then arises: how does evaporator efficiency play into emissions reduction compared with changing the input concentration? Due to the hyperbolic decay of energy demand shown in Figure 2, we can see that as input concentrations get higher, their relative reduction

becomes less. For example, you are only decreasing the necessary energy by 0.5% when you go from 19 to 20 °Bx input sap. So, as you get to higher input concentrations, it may be more cost effective to make your evaporator more efficient, as sizing up your RO unit will cost more for a given marginal energy reduction.

Utilizing the Model

Sugarmakers can use this model before the season to calculate how much energy and fuel they may need based on how much sap they expect to collect, what the average °Bx will be, whether they will concentrate the sap with RO, what °Bx they are bringing it to, and how efficient their evaporator is. Using only starting and ending °Bx, one can see how much sap they will need per gallon of syrup, and can calculate the boiling point temperature, change in enthalpy, change in mass, and change in specific heat for the solution on a °Bx by °Bx stepwise basis. Summing the energy needed to bring to a boil and change phases from starting °Bx to ending °Bx gives you the total energy for making a single gallon of syrup. One can then divide how much sap is collected over the course of the year and divide it by how much sap is needed to make one gallon of syrup to get the total amount of syrup produced over the course of a year. Multiplying this number by the energy calculated for one gallon gives you the total energy for the season. Knowing the efficiency of the evaporator, one can calculate what the actual energy use will be based on these non-ideal conditions. Knowing how much energy you need, one can divide this by the heat content of the evaporator fuel to calculate the expected quantity of fuel, and subsequent cost.

Conclusion

While current rules-of-thumb are sufficient for rough estimates of energy consumption in the boiling process using traditional methods, more exact calculation methods can provide better guidance for producer decision-making. As technology has advanced and RO concentration becomes more popular, sugarmakers can use this thermodynamic model to correctly size reverse osmosis units for their operations based on cost and energy. Additionally, by using the modified Jones Rule described above, producers can make more exact calculations with a wide range of concentrated sap inputs and variable °Bx outputs. In the long run, using these more exact methods of calculation for the most cost-intensive stage in the syrup making process can save significant amounts of money for producers.

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