

# **Modeling Loss of Volatile Compounds of Industrially Processed Orange Juice**

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Final Report and Model

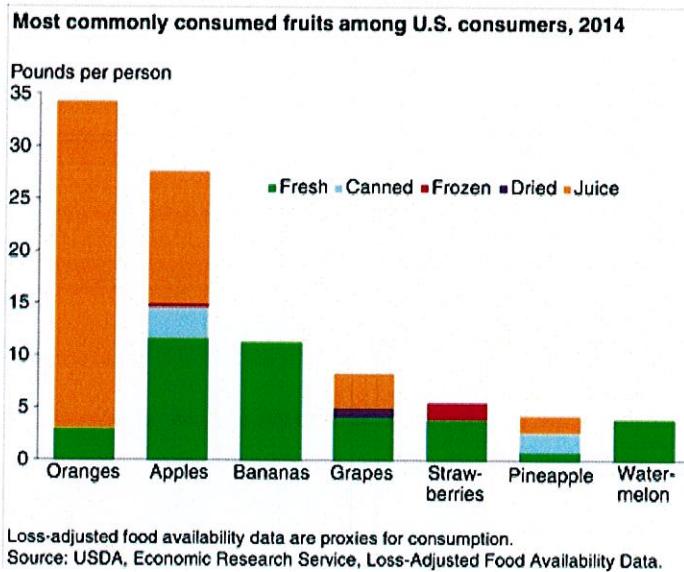
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## Introduction and System Description

Orange juice is the most widely consumed fruit product in the United States according to a study performed by the United States Department of Agriculture Economic Research Service. With such immense levels of consumption, preventing product waste becomes a key factor in sustainability for both the economy and the environment.

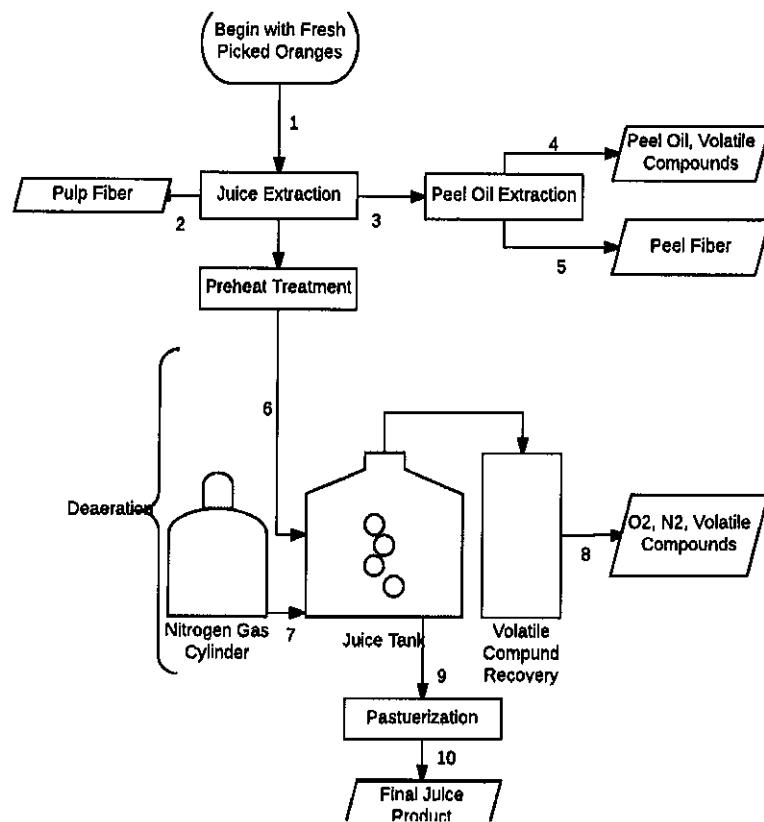


Over the past century, there have been many advancements to improve the food safety, quality, and processing efficiency of industrially pressed orange juice, shown in the Juice Processing Diagram below. Many of these processes, however, have proven to decrease the organoleptic quality of the product as compared to freshly home-squeezed orange juice. Over the course of processing oranges, volatile compounds responsible for aroma and flavor are evaporated and ascorbic acid is degraded, causing the juice to become more bitter and tasteless. Studies have shown that deaeration is the step primarily responsible for the loss of volatile compounds in orange juice production (M.J. Jordan, et al., 2003).

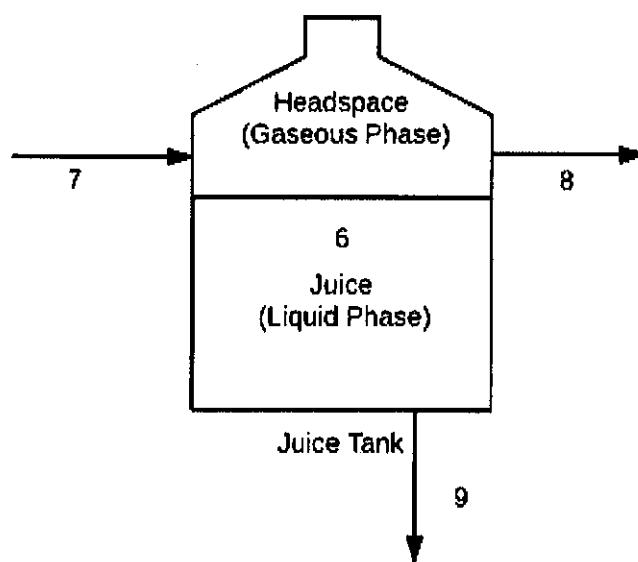
The purpose of deaeration is to strip the product of dissolved oxygen to reduce possible chemical, enzymatic, and microbial reactions that can decrease the shelf-life of orange juice. Oxygen is often in intercellular spaces within fruits that become integrated into the juice upon pressing. There are multiple methods of deaeration, including static and vacuum headspace methods, but the most efficient is nitrogen sparging. In this method, nitrogen is bubbled up through a batch tank of orange juice in order to replace nitrogen with oxygen by creating a driving force for mass transfer. To estimate the effectiveness and organoleptic cost of deaeration, a model can be used.

The purpose of this model is to estimate the organoleptic quality of orange juice after processing. Organoleptic quality will be determined by the concentrations of oxygen, nitrogen, volatile compounds, ascorbic acid, and 2,3-diketogulonic acid.

*Juice Processing Diagram*



*Isolated System of Interest*



	6 (Liquid)	7 (Gas)	8 (Gas)	9 (Liquid)
Juice (Water + Misc.)	✓		✓	✓
Oxygen	✓		✓	✓
Nitrogen	✓	✓	✓	✓
Volatile Compounds	✓		✓	✓
Ascorbic Acid	✓			✓

#### Areas of Energy Transfer:

- Preheat Treatment: Juice heated to a specified temperature
- Deaeration Juice Tank: Temperature change over time in the tank due to conduction

## Model

The model is based off transient thermal conduction, convective mass transfer, transient thermal conduction, and reaction kinetics.

The first step in the model is to determine the temperature profile as a function of time. Many variables, including saturated vapor pressures, Henry's Law constants, and reaction rate constants, are dependent on temperature. The following program was used to determine the temperature profile. The derivation for these equations can be found in Iteration 3 of the design process appendix.

#### Determining Temperature Profile

$$k := .5984$$

$$\rho := 997.1 \quad \text{Water Properties}$$

$$c := 4180$$

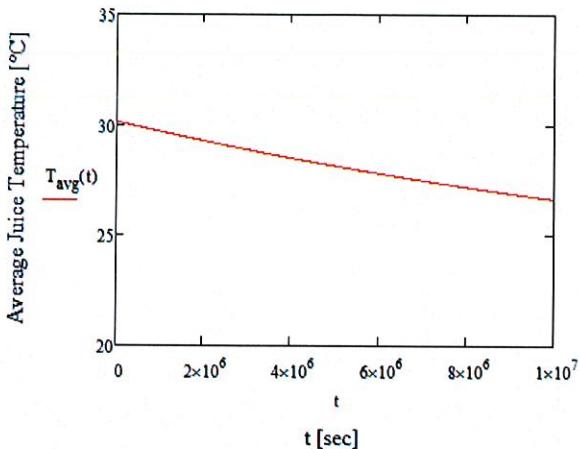
$$r := \frac{D_T}{2}$$

$$\alpha := \frac{k}{c \cdot \rho}$$

$$T(x, t) := \frac{4}{\pi} \cos\left(\pi \cdot \frac{x}{2r}\right) \cdot e^{-\left[\alpha \cdot \left(\frac{\pi}{2r}\right)^2 \cdot t\right]} \cdot (T_i - T_s) + T_s$$

$$T_{avg}(t) := \int_0^r \frac{1}{r} \cdot T(x, t) dx$$

Example output for this portion of the program is shown below.



The next step is the determine the initial concentrations of all the components in both the juice and the headspace. The following portion of program was used.

#### Determining Vapor Pressure Functions

$$M_{VCi} := \frac{CVC_i}{.136283} = 5.136 \times 10^{-3} \text{ mol/L}$$

$$mol_{VCi} := M_{VCi} \cdot V_L = 2.568 \text{ mol}$$

$$M_W := \frac{CW_i}{.018015} = 49.292 \text{ mol/L}$$

$$mol_W := M_W \cdot V_L = 2.465 \times 10^4 \text{ mol}$$

$$M_{SSi} := \frac{CSS_i}{.3423} = 0.345$$

$$M_{Ai} := \frac{CA_i}{.0391} = 76.726$$

$$mol_{SS} := M_{SSi} \cdot V_L = 172.363$$

$$mol_A := M_{Ai} \cdot V_L = 3.836 \times 10^4$$

$$SVP_{Wi} := \frac{2338.8}{101325} \text{ atm}$$

$$SVP_{VCI} := \frac{190}{101325} \text{ atm}$$

$$SVP_W(t) := SVP_{Wi} \exp \left[ \frac{2265 \cdot 10^3}{18.015 \cdot 8.314} \left( \frac{1}{T_{avg}(t) + 275} - \frac{1}{25 + 273} \right) \right] \text{ atm}$$

$$SVP_{VC}(t) := SVP_{VCI} \exp \left[ \frac{45.9 \cdot 10^3}{8.314} \left( \frac{1}{T_{avg}(t) + 275} - \frac{1}{302} \right) \right] \text{ atm}$$

$$P_{WSi} := \frac{mol_W}{(mol_W + mol_{VC} + mol_{SS} + mol_A)} \cdot SVP_W(0) = 2. atm \times 10^{-3} \quad \text{atm}$$

$$P_{VCSI} := \frac{mol_{VC}}{(mol_W + mol_{VC} + mol_{SS} + mol_A)} \cdot SVP_{VC}(0) = 6.328 \times 10^{-8} \quad \text{atm}$$

### Determining Initial Partial Pressures in Headspace

$$P_{NHi} := \frac{XA_N}{100} \cdot P_{total} = 0$$

$$P_{OHi} := \frac{XA_O}{100} \cdot P_{total} = 0.99$$

$$P_{VCHi} := 0$$

$$P_{WHi} := \frac{RH}{100} \cdot SVP_W(0)$$

### Surface Gas Partial Pressures

$$K_N(t) := 6.5 \cdot 10^{-4} \cdot e^{-1300 \left( \frac{-1}{293.15} + \frac{1}{T_{avg}(t)+273} \right)} \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

$$K_O(t) := 1.3 \cdot 10^{-3} \cdot e^{-1700 \left( \frac{-1}{293.15} + \frac{1}{T_{avg}(t)+273} \right)} \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

Derivations for these portions of the program can be found in Iterations 4 and 5 of the appendix. The next portion determined the convective mass transfer coefficients based on the properties of the components and the Reynolds Number based on the velocity generated by flowing nitrogen over the surface of the liquid. The derivations for convective mass transfer can be found in Iteration 4 of the appendix.

## Determining Convective Mass Transfer Coefficients

$$D_{VC} := 0.1 \frac{\text{cm}^2}{\text{s}}$$

$$D_N := 0.176 \frac{\text{cm}^2}{\text{s}}$$

$$D_O := 0.176 \frac{\text{cm}^2}{\text{s}}$$

$$D_W := 0.282 \frac{\text{cm}^2}{\text{s}}$$

$$Re := \frac{D_T \cdot V_{in} \cdot 10^{-3}}{1.76 \cdot 10^{-5}} = 284.091$$

$$Sc_N := 280$$

$$Sc_O := 400$$

$$Sc_W := 340$$

$$Sc_{VC} := 500$$

## Assuming Laminar Flow

$$h_N := \frac{D_N}{D_T} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_N^{-\frac{1}{3}} \right) = 2.577$$

$$h_O := \frac{D_O}{D_T} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_O^{-\frac{1}{3}} \right) = 2.903$$

$$h_{VC} := \frac{D_{VC}}{D_T} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_{VC}^{-\frac{1}{3}} \right) = 1.777$$

$$h_W := \frac{D_W}{D_T} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_W^{-\frac{1}{3}} \right) = 4.406$$

Next, the second order reaction rate for the decomposition of ascorbic acid into 2,3-diketogulonic acid was determined based off the temperature profile. Derivations for this portion of the program can be found in Iteration 5 of the appendix.

## Determining Reaction Coefficients

$$k_1 := 2.38 \cdot 10^{-4} \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

$$E := -1.3903 \cdot \text{pH} + 17.2464 = 11.685$$

$$K_1(t) := k_1 \cdot \exp \left[ \left( \frac{1}{33 + 273} + \frac{1}{T_{avg}(t) + 273} \right) \cdot \frac{E}{0.08206} \right]$$

Lastly, a series of ordinary differential equations was solved using the MathCad Odesolve function as shown below. Derivations of this portion can be found in Iterations 4 and 5 of the appendix.

**Given**

$$\text{CNL}'(t) = \frac{-h_N \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ \frac{\text{CNL}(t)}{K_N(t) \cdot 0.08206 \cdot (T_{avg}(t) + 273)} - \text{CNH}(t) \right]$$

$$\text{COL}'(t) = \frac{-h_O \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ \frac{\text{COL}(t)}{K_O(t) \cdot 0.08206 \cdot (T_{avg}(t) + 273)} - \text{COH}(t) \right] - K_1(t) \cdot \text{CAAL}(t) \cdot \text{COL}(t)$$

$$\text{CVCL}'(t) = \frac{-h_{VC} \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ \text{SVP}_{VC}(t) \cdot \frac{\text{CVCL}(t) \cdot V_L}{\text{CVCL}(t) \cdot V_L + \text{CWL}(t) \cdot V_L + mol_{SS} + mol_A} \cdot \frac{1}{0.08206 \cdot (T_{avg}(t) + 273)} - \text{CVCH}(t) \right]$$

$$\text{CWL}'(t) = \frac{-h_W \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ \text{SVP}_W(t) \cdot \frac{\text{CWL}(t) \cdot V_L}{\text{CVCL}(t) \cdot V_L + \text{CWL}(t) \cdot V_L + mol_{SS} + mol_A} \cdot \frac{1}{0.08206 \cdot (T_{avg}(t) + 273)} - \text{CWH}(t) \right]$$

$$\text{CAAL}'(t) = -2K_1(t) \cdot \text{CAAL}(t) \cdot \text{COL}(t)$$

$$\text{CDKGL}'(t) = 2K_1(t) \cdot \text{CAAL}(t) \cdot \text{COL}(t)$$

$$\text{CNL}(0) = \text{CN}_i$$

$$\text{COL}(0) = \text{CO}_i$$

$$\text{CVCL}(0) = M_{vci}$$

$$\text{CWL}(0) = M_w$$

$$\text{CAAL}(0) = \text{CAA}_i$$

$$\text{CDKGL}(0) = 0$$

$$\text{CNH}'(t) = \frac{V_{in}}{V_H} \cdot \frac{P_{total}}{0.08206 \cdot (T_{avg}(t) + 273)} - \frac{V_L}{V_H} \cdot \text{CNL}'(t) - \frac{V_{in}}{V_H} \text{CNH}(t)$$

$$\text{COH}'(t) = \frac{-V_L}{V_H} \cdot \text{COL}'(t) - \frac{V_{in}}{V_H} \text{COH}(t)$$

$$\text{CVCH}'(t) = \frac{-V_L}{V_H} \cdot \text{CVCL}'(t) - \frac{V_{in}}{V_H} \text{CVCH}(t)$$

$$\text{CWH}'(t) = \frac{-V_L}{V_H} \cdot \text{CWL}'(t) - \frac{V_{in}}{V_H} \text{CWH}(t)$$

+

$$\text{CNH}(0) = \frac{P_{\text{NH}_i}}{[0.08206 \cdot (T_{\text{avg}}(0) + 273)]}$$

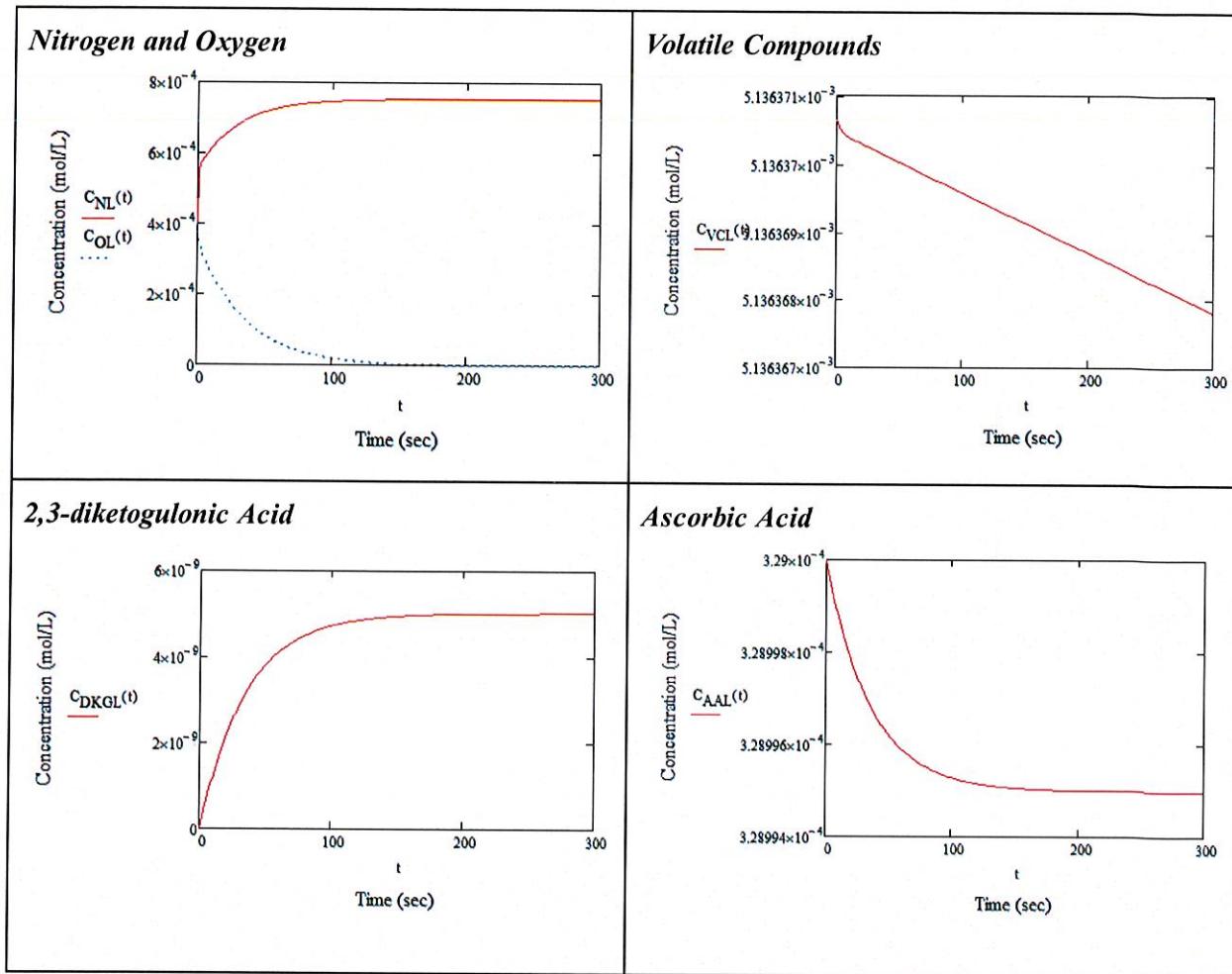
$$\text{COH}(0) = \frac{P_{\text{OH}_i}}{[0.08206 \cdot (T_{\text{avg}}(0) + 273)]}$$

$$\text{CVCH}(0) = \frac{P_{\text{VCH}_i}}{[0.08206 \cdot (T_{\text{avg}}(0) + 273)]}$$

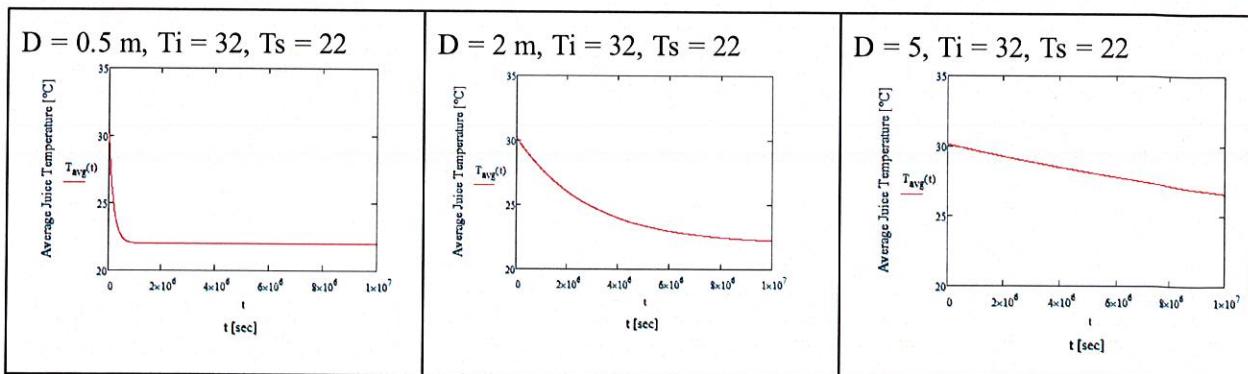
$$\text{CWH}(0) = \frac{P_{\text{WCH}_i}}{[0.08206 \cdot (T_{\text{avg}}(0) + 273)]}$$

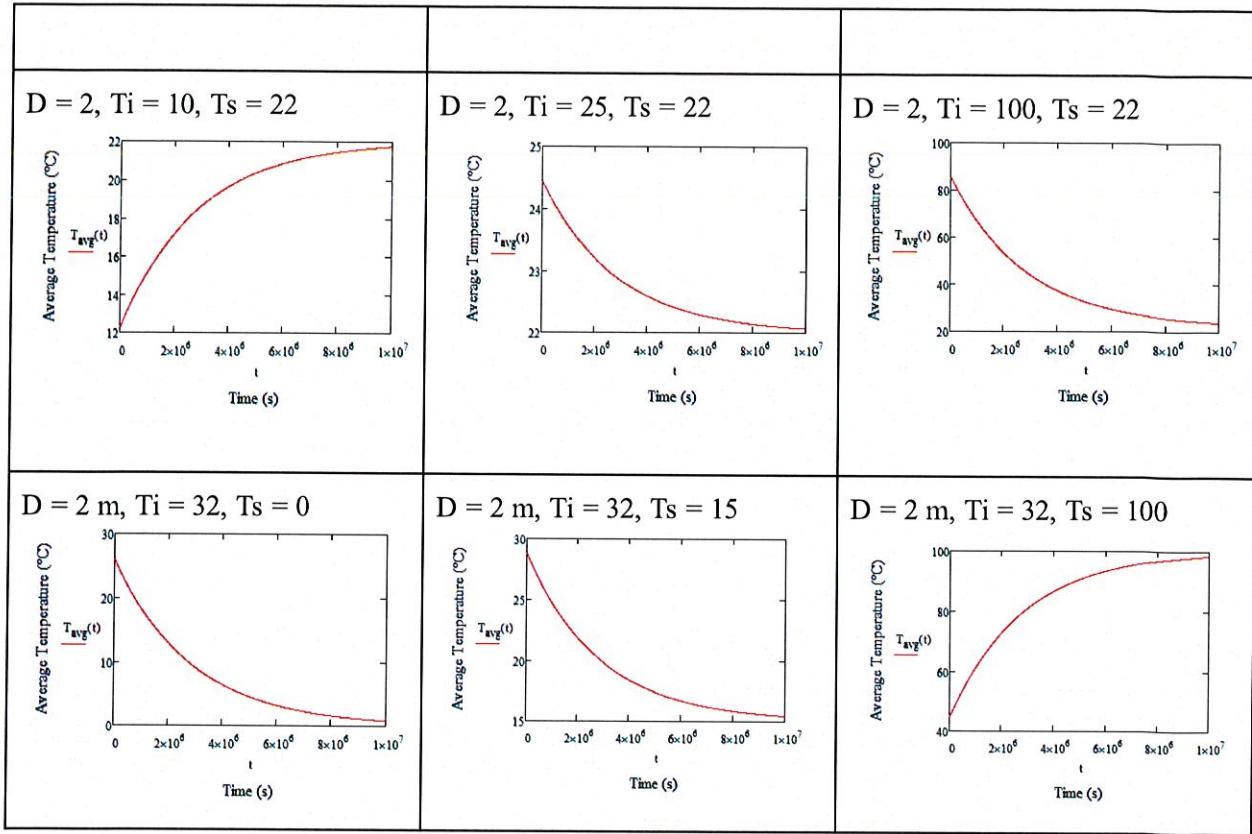
Below are example model parameters with an example model output.

***Input Parameters*****USER INPUTS****Temperature Initial Conditions** $T_s := 22$  Input Surface Temperature of Tank ( $T_s$ ) $T_i := 32$  Input Initial Temperature of the Juice ( $T_i$ )**Initial Composition of Air In Headspace** $X_{A_N} := 78\%$  Input Ratio of Nitrogen in the Air (Typically 0.78) $X_{A_O} := 21\%$  Input Ratio of Oxygen in the Air (Typically 0.21) $RH := 20\%$  Input Relative Humidity $P_{total} := 1 \text{ atm}$  Input Total Pressure in the Headspace**Initial Concentrations in Liquid** $CVC_i := 7 \cdot 10^{-4} \frac{\text{kg}}{\text{L}}$  Input Initial Concentration of Volatile Compounds in Juice $CW_i := .888 \frac{\text{kg}}{\text{L}}$  Input Initial Concentration of Water in Juice $CAA_i := 3.29 \cdot 10^{-4} \frac{\text{kg}}{\text{L}}$  Input Initial Concentration of Ascorbic Acid in Juice $CSS_i := .118 \frac{\text{kg}}{\text{L}}$  Input Concentration of Soluble Solids in Juice $CA_i := 3.0 \frac{\text{kg}}{\text{L}}$  Input Concentration of Ash in Juice $CN_i := 4 \cdot 10^{-4} \frac{\text{mol}}{\text{L}}$  Input Initial Concentration of Nitrogen in Juice $CO_i := 4 \cdot 10^{-4} \frac{\text{mol}}{\text{L}}$  Input Initial Concentration of Oxygen in Juice $pH := 4$  Input the pH of the Juice**Tank Volumes** $V_H := 50 \text{ L}$  Input Total Air Volume in the Headspace $V_L := 500 \text{ L}$  Input Total Juice Volume $D_T := 2 \text{ m}$  Input Diameter of Tank $V_{in} := 2 \frac{\text{L}}{\text{s}}$  Input Volumetric Flow Rate of Nitrogen in Headspace

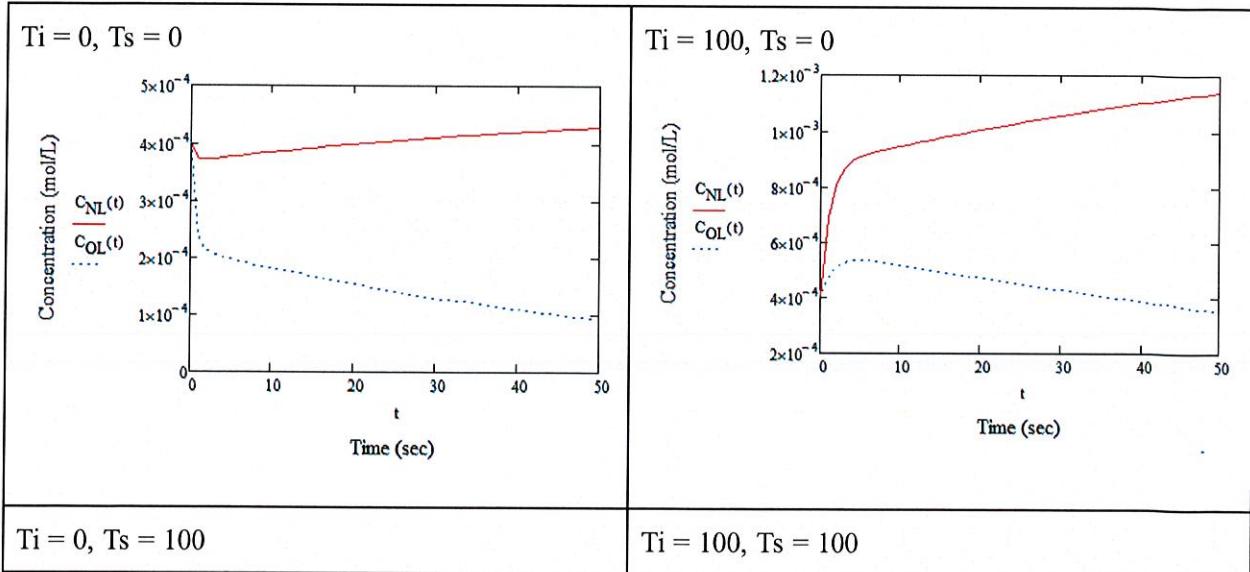
**System Output****Analysis**

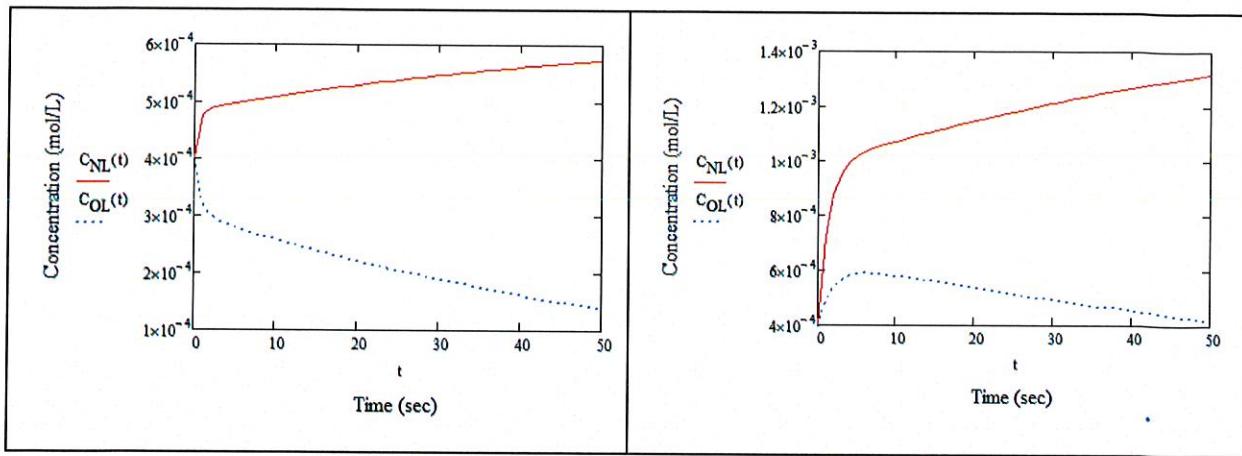
The first portion of the program creates a temperature profile. The primary factors that affect this profile are the diameter- which is the characteristic length for thermal conduction-, the initial temperature of the juice, and the surface temperature of the tank. The temperature profiles below demonstrate the dependence on each.



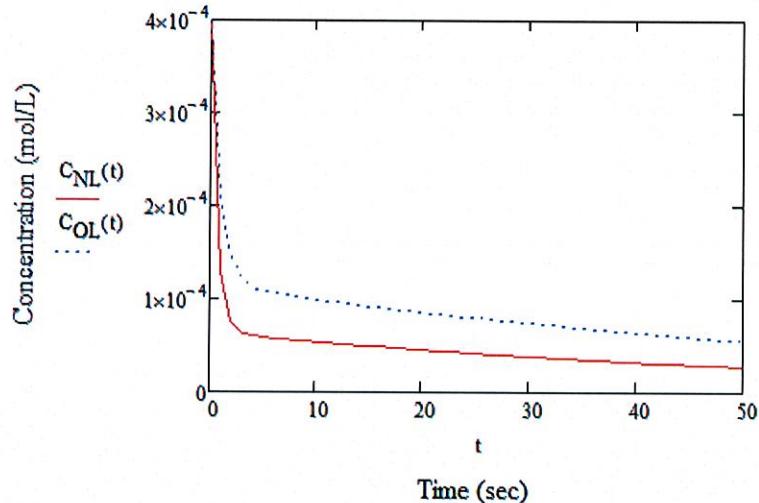


As can be seen by these examples, the shape of the curves are dependent on the diameter of the tank while the direction and scale of the curves are dependent on the initial temperature and the surface temperature. It should be noted that boiling and freezing effects are not considered this model as it lies outside average operating parameters. Example oxygen concentrations over time are given below for specified initial and surface temperatures.



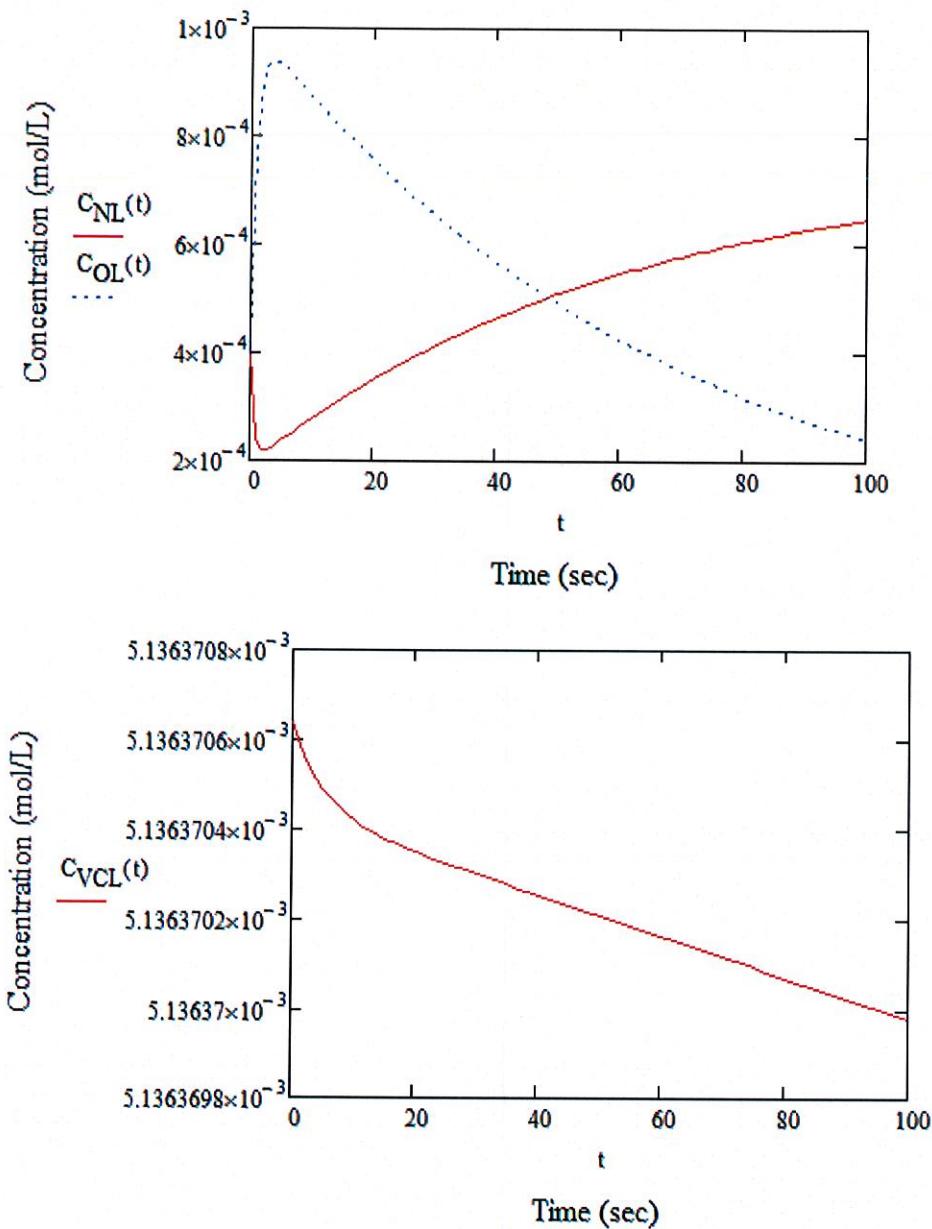


Other factors influencing the model are the headspace pressure and the nitrogen volumetric flow rate. The operation can be run under vacuum conditions by setting the pressure to 0 atm. An example is shown below.



There is accumulation of all species in the headspace under these conditions, which is expected. One limitation to the model is that there needs to be a nitrogen flow rate of greater than  $1 \times 10^{-15}$  L/s for there to be evident evaporation of the volatile compounds. This is because the model is based on convective mass transfer, so without a flow rate, the model predicts a change in concentration of 0.

Other model factors include initial concentrations of the juice and the headspace. Under standard operating conditions, there is typically a drive toward equilibrium, followed by a more constant rate of change. So, when there is a large initial concentration of oxygen in the air before the nitrogen flow begins, a output like the following is given where two phases are evident.



This proves that the model follows expected trends for changes in initial concentrations.

## Conclusion and Future Analysis

Overall, the model is effective at demonstrating the expected trends at varying pressures, flow rates, and headspace and juice compositions. However, since it is a convective mass transfer model, a volumetric flow rate of nitrogen must be present for the mass transfer to be demonstrated.

One large assumption made for this model was the method of nitrogen flow. In production, nitrogen gas would be bubbled through the system rather than blown across the surface. However, this leads to a complex system of partial differential equations where the mass flux over the nitrogen bubble would be shown as

$$mNB'(\theta, t) = h_N^{-3} \cdot \frac{3 \cdot (mNB(\theta) + mOB(\theta) + nVCB(\theta) + nWB(\theta)) \cdot \frac{0.08206 \cdot (T_{avg}(t) + 273)}{P[H_T - (\theta \cdot u_{inf})]}^{\frac{-1}{3}}}{4 \cdot \pi}$$

$$\cdot (mNB(\theta) + mOB(\theta) + nVCB(\theta) + nWB(\theta)) \cdot \frac{0.08206 \cdot (T_{avg}(t) + 273)}{P[H_T - (\theta \cdot u_{inf})]} \left[ mNB(\theta) \cdot K_N(t) \cdot 0.08206 \cdot (T_{avg}(t) + 273) - \frac{CNL(t)}{1000} \right]$$

Where  $\theta$  is the time that the bubble has been rising, the volume is being approximated as a function of the total moles of the diffusing species, and the convective mass transfer coefficient is based on the equation

$$h_N := \left[ 2 + \left( 0.4 \cdot Re^{0.5} + 0.06 Re^{0.3} \right) \cdot Sc_N^{0.4} \right] \cdot \frac{D_N}{D_B}$$

And the pressure is given as

$$P(h) := 1000 \cdot 9.8 \cdot h$$

Where  $h$  is the distance from the top of the liquid. Comsol may be helpful in evaluating these functions in future models.

In conclusion, though the time scale for the model may be inaccurate compared to the time scale of nitrogen bubbling, the model still shows appropriate, clear trends for the concentrations of oxygen, nitrogen, volatile compounds, ascorbic acid, and 2,3-diketogulonic acid.

## Appendix A: Design Process

### *Design Summary*

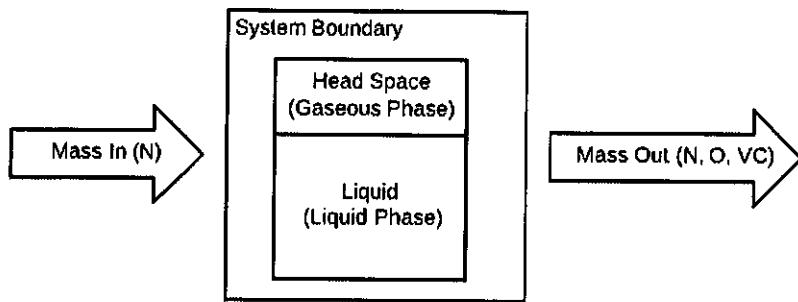
The first iteration of this is a steady state mass balance where there are known concentrations leaving the system. Since it was assumed that the mass transfer, and thus the exiting stream, was at a constant rate and composition, the concentrations fell below zero. This model can be used if the concentration leaving as a function of time is known. In iteration 2, this error was countered by creating a constant concentration in the headspace and modeling the mass transfer as a function of surface concentration and concentration in the juice. Many of the parameters in this model were dependent on temperature, so an energy balance was performed in the third iteration assuming constant wall temperatures. Once these parameters were set, the concentration changes in the headspace could be considered in the fourth iteration. Instead of modeling the mass transfer as a function of the juice concentration, it was modeled as a function of surface concentration and headspace concentration with a constant flow rate of nitrogen entering the system. The surface concentrations were dependent on the juice concentrations, so a system of ordinary differential equations had to be solved. This iteration follows the expected change in concentrations much more accurately. Analysis of iteration 4 showed that modeling a mass flow rate of nitrogen was a driving force for oxygen removal. In the fifth and final iteration, the consumption of oxygen and ascorbic acid to create 2,3-diketogulonic acid was included in the model.

### Iteration 1: Overall Mass Balance

#### *Simplifying Assumptions*

- Assumption 1: It is assumed that all the volatile compounds can be lumped together and all share the properties of limonene since limonene constitutes about 80% of the total volatile compound concentration.
  - This were selected due to the research done by M.J. Jordan, et al., 2003.
- Assumption 2: There is no preheating step so there is no change in temperature over deaeration.
  - A preheating step before deaeration to decrease initial oxygen concentrations is typical in the industry. The change in temperature of the juice in the deaeration tank will impact nitrogen sparging efficiency.
- Assumption 3: No mass is accumulated over deaeration.
  - This statement must be analyzed for accuracy. There will be some mass loss to evaporation.
- Assumption 4: No chemical reactions or energy transfers are occurring over deaeration.
  - In the real system, ascorbic acid reacts with oxygen to decompose over time.
- Assumption 5: Instead of nitrogen sparging with bubbles from the bottom, the surface of the tank is flushed with nitrogen.
  - This allows for a simplified model

#### *Diagram*



### **Total Mass Balance**

In this system, the juice mass remains the same but nitrogen gas is being added to the system in order to extract oxygen and, consequently, volatile compounds. Thus

$$M_{in} - M_{out} + M_{gen} - M_{con} = M_{acc}$$

Simplifies to

$$M_{in} - M_{out} = 0$$

Since there is no mass being consumed or generated and it is assumed that the mass accumulated is 0.

### **Component Mass Balance**

Nitrogen:

$$M_{in} - M_{out} = M_{acc}$$

Oxygen:

$$-M_{out} = M_{acc}$$

Volatile Compounds:

$$-M_{out} = M_{acc}$$

### **Combination**

Adding this back to the overall mass balance, this becomes

$$M_{N,in} - M_{N,out} - M_{O,out} - M_{VC,out} = M_{N,acc} + M_{O,acc} + M_{VC,acc} = 0$$

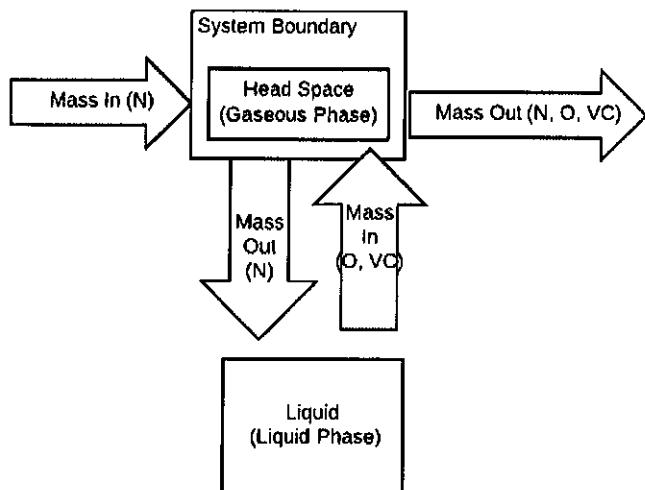
There is no chemical reaction from which a reaction rate can be determined but it is known that nitrogen accumulates in the system due to the equilibrium of partial pressures and concentrations. In order to do this, a new system must be defined.

### **Headspace Mass Balance**

#### **Simplifying Assumptions:**

- Assumption 1: The headspace is at steady state.

#### **Diagram**



### ***Overall Mass Balance:***

Because this system is assumed to be steady state and there is no generation or consumption, the mass balance equation can be written as:

$$M_{in} - M_{out} = 0$$

### ***Component Mass Balance:***

Nitrogen:

$$M_{N,1} - M_{N,2} - M_{N,3} = 0$$

Oxygen:

$$M_{O,2} - M_{O,3} = 0$$

Volatile Compounds:

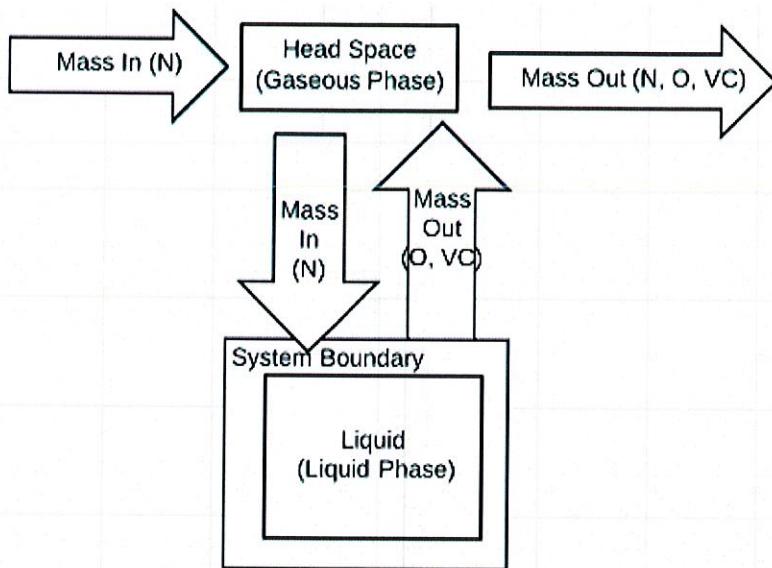
$$M_{VC,2} - M_{VC,3} = 0$$

### **Liquid Mass Balance**

#### ***Simplifying Assumptions:***

- Assumption 1: Though the composition changes with time, the total mass does not.
- Assumption 2: All mass transfer occurs in one direction. For example, nitrogen only enters the system, it does not exit.
- Assumption 3: Water is not lost in the system.

***Diagram:***



### **Overall Mass Balance:**

Since there are no chemical reactions occurring and the accumulation of the overall system is assumed to be 0:

$$M_{in} - M_{out} = 0$$

### **Component Mass Balance:**

Nitrogen:

$$M_{in} = M_{acc}$$

Oxygen:

$$-M_{out} = M_{acc}$$

Volatile Compounds:

$$-M_{out} = M_{acc}$$

Combining the headspace mass balances for iteration 1 and applying it to the liquid system, the mass balance equation expands to:

$$(M_{N,in} - M_{N,out}) - M_{O,out} - M_{VC,out} = M_{N,acc} + M_{O,acc} + M_{VC,acc} = 0$$

Which is the same as the overall mass balance. Converting this to concentration, this model becomes that shown below.

### **Input Parameters**

$$CN_i := 0 \frac{\text{kg}}{\text{L}} \quad M_{in}(t) := 1.251 \cdot 10^{-3}(t) \text{ kg}$$

$$CO_i := 1 \cdot 10^{-5} \frac{\text{kg}}{\text{L}} \quad X_N := .4 \% \text{ mass of stream}$$

$$CVC_i := 7 \cdot 10^{-4} \frac{\text{kg}}{\text{L}} \quad X_O := .3 \% \text{ mass of stream}$$

$$V := 500 \text{ L} \quad X_{vc} := .3 \% \text{ mass of stream}$$

**Mass Balance Equations**

$$M_{\text{out}}(t) := M_{\text{in}}(t) \quad \text{kg}$$

$$N_{\text{in}}(t) := M_{\text{in}}(t) \quad \text{kg}$$

$$O_{\text{out}}(t) := X_O \cdot M_{\text{out}}(t) \quad \text{kg}$$

$$VC_{\text{out}}(t) := X_{vc} \cdot M_{\text{out}}(t) \quad \text{kg}$$

$$N_{\text{out}}(t) := X_N \cdot M_{\text{out}}(t) \quad \text{kg}$$

$$Acc_N(t) := N_{\text{in}}(t) - N_{\text{out}}(t) \quad \text{kg}$$

$$Acc_O(t) := -O_{\text{out}}(t) \quad \text{kg}$$

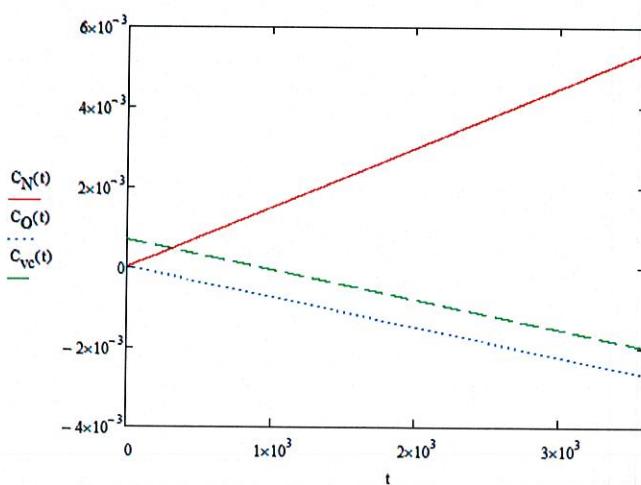
$$Acc_{vc}(t) := -VC_{\text{out}}(t) \quad \text{kg}$$

**Converting to Concentration**

$$C_N(t) := CN_i + \frac{Acc_N(t)}{V} \quad \frac{\text{kg}}{\text{L}}$$

$$C_O(t) := CO_i + \frac{Acc_O(t)}{V} \quad \frac{\text{kg}}{\text{L}}$$

$$C_{vc}(t) := CVC_i + \frac{Acc_{vc}(t)}{V} \quad \frac{\text{kg}}{\text{L}}$$

**Plot of Program Output**

While this could serve as a simple model if the composition of the exit stream is known as a function of time, both the volatile compound and oxygen concentrations drop below 0, making this model infeasible. The relationship between the exit stream composition and the concentrations of the liquid must be analyzed further.

## Iteration 2: Transient Mass Diffusion

### Assumptions Addressed

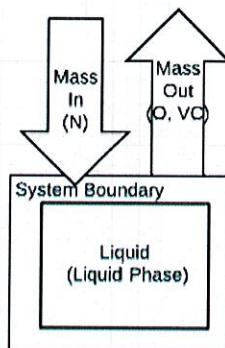
- The mass flow out of the system is dependent on the outlet concentration.

For this iteration, it is assumed that the concentration is now dependent on transient mass diffusion into and out of the fluid.

### Simplifying Assumptions:

- Assumption 1: The surface of the fluid is in equilibrium with the partial pressure of each component in the air.
  - This assumption is reasonable as it only defines the concentration in the liquid of a differential volume at  $z = L$ . Over time, the assumption becomes negligible.
- Assumption 2: The partial pressures in the air are not changing over time.
  - This would indicate that there is no applied nitrogen gradient. This is a significant assumption that will affect the overall mass balance
- Assumption 3: Mass flow is one directional, and the bottom of the tank is impermeable.
  - This is a reasonable assumption as the only exposed surface will be the top of the tank.
- Assumption 6: There are no solvents or ash in the juice.
  - This is used to simplify calculations for saturated vapor pressure.

### Diagram:



### Vapor-Gas Equilibrium

Since limonene is lost to evaporation, it is known that at the surface of the liquid limonene has a partial pressure proportional to its saturated vapor pressure of 190 Pa and the composition of the fluid. It is assumed that vapors are one percent of the total pressure

$$P_w := \frac{mol_w}{(mol_w + mol_{vc})} \cdot SVP_w = 2.339 \times 10^3 \text{ Pa}$$

$$P_{vc} := \frac{mol_{vc}}{(mol_w + mol_{vc})} \cdot SVP_{vc} = 0.018 \text{ Pa}$$

$$P_{\text{total}} = (P_w + P_{vc}) \cdot 100 \quad \text{Pa}$$

$$P_N := \frac{(P_{\text{total}} \cdot X_{A_N})}{101325} \quad \text{atm}$$

$$P_O := \frac{(P_{\text{total}} \cdot X_{A_O})}{101325} \quad \text{atm}$$

Where SVP stands for saturated vapor pressure. If it is assumed that the fluid begins in equilibrium with the air, then the initial nitrogen and oxygen levels can be determined using Henry's Law.

$$K_N := 6.5 \cdot 10^{-4} \quad \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

$$K_O := 1.3 \cdot 10^{-3} \quad \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

$$CN_s := K_N \cdot P_N = 1.17 \times 10^{-3} \quad \frac{\text{mol}}{\text{L}}$$

$$CO_s := K_O \cdot P_O = 6.301 \times 10^{-4} \quad \frac{\text{mol}}{\text{L}}$$

### **Mass Balance with Diffusion**

The overall mass balance for a system with mass transfer is

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} + r$$

Where the first term is accumulation, the second term is convection, the third term is conduction, and the last term is The component mass balance becomes

$$\begin{aligned} M_{\text{in}} &= M_{\text{acc}} \\ \frac{\partial C}{\partial t} &= D \frac{\partial^2 C}{\partial x^2} \end{aligned}$$

By converting concentration to a dimensionless concentration  $\theta$  and using the separation of variables method, two ordinary differential equations are found.

$$\begin{aligned} \theta(x, t) &= F(x)G(t) = \frac{C(t) - C_s}{C_i - C_s} \\ F''(x) + p^2 F(x) &= 0 \\ G'(t) + D \cdot p^2 G(t) &= 0 \end{aligned}$$

By solving these ODEs analytically, the solution becomes

$$\frac{c - c_s}{c_i - c_s} = \sum_{n=0}^{\infty} \frac{4(-1)^n}{(2n+1)\pi} \cos \frac{(2n+1)\pi x}{2L} e^{-D \left( \frac{(2n+1)\pi}{2L} \right)^2 t}$$

Since there is no driving force for diffusion yet integrated into the model, it is predicted that the time needed for the solution concentration to approach the surface concentration will be large, and at large time intervals, the summation can be ignored so that the equations for the concentration of volatile compounds (CVC), nitrogen (CN), and oxygen (CO) are those given below.

$$CVC(x, t) := \frac{4}{\pi} \cos\left(\pi \cdot \frac{x}{2L}\right) \cdot e^{-D_{VC}\left(\frac{\pi}{2L}\right)^2 \cdot t} \cdot (CVC_i - CVC_s) + CVC_s$$

$$CN(x, t) := \frac{4}{\pi} \cos\left(\pi \cdot \frac{x}{2L}\right) \cdot e^{-D_N\left(\frac{\pi}{2L}\right)^2 \cdot t} \cdot (CN_i - CN_s) + CN_s$$

$$CO(x, t) := \frac{4}{\pi} \cos\left(\pi \cdot \frac{x}{2L}\right) \cdot e^{-D_O\left(\frac{\pi}{2L}\right)^2 \cdot t} \cdot (CO_i - CO_s) + CO_s$$

To find the average concentration, the integral over the characteristic length of diffusion divided by the characteristic length of diffusion is taken.

$$CVC_{avg}(t) := \int_0^L \frac{1}{L} \cdot CVC(x, t) dx$$

$$CN_{avg}(t) := \int_0^L \frac{1}{L} \cdot CN(x, t) dx$$

$$CO_{avg}(t) := \int_0^L \frac{1}{L} \cdot CO(x, t) dx$$

### Model Example:

#### Input Parameters

$$L := 100 \text{ cm}$$

$$XA_N := .78 \text{ %}$$

$$CN_i := 0$$

$$XA_O := .21 \text{ %}$$

$$CO_i := 3.125 \cdot 10^{-4}$$

$$XA_{vapor} := .01 \text{ %}$$

$$CVC_i := 7 \cdot 10^{-4} \frac{\text{kg}}{\text{L}}$$

$$V := 500 \text{ L}$$

#### Material Properties

$$SVP_W := 2338.8 \text{ Pa}$$

$$K_N := 6.5 \cdot 10^{-4} \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

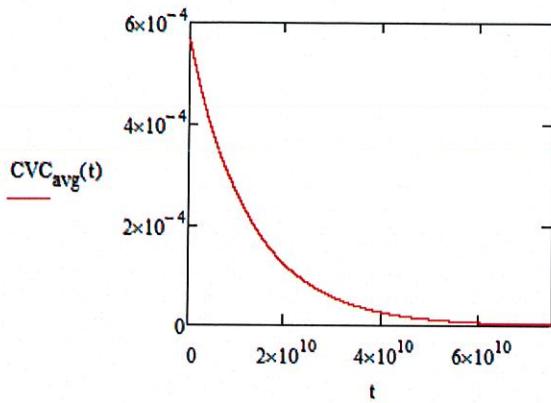
$$D_{VC} := 10^{-6.5} \frac{\text{cm}^2}{\text{s}}$$

$$SVP_{VC} := 190 \text{ Pa}$$

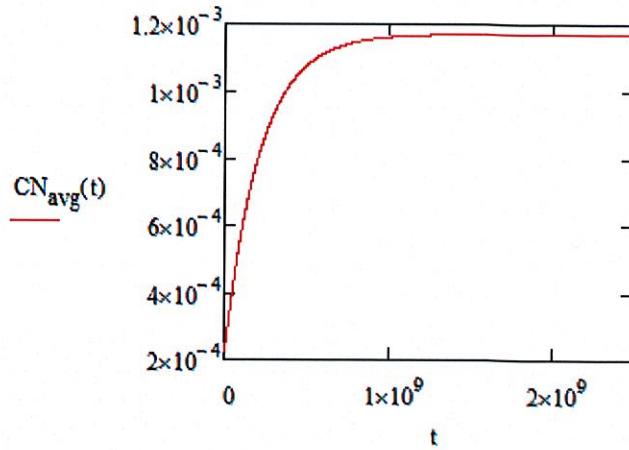
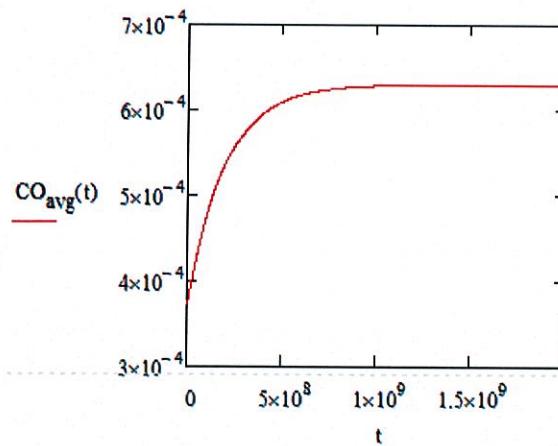
$$K_O := 1.3 \cdot 10^{-3} \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

$$D_N := 1.88 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}$$

$$D_O := 2.03 \cdot 10^{-5} \frac{\text{cm}^2}{\text{s}}$$



The concentrations are in mol/L and time is in seconds. These plots more closely resemble the expected results than the first iteration. However, the time frame is far longer than that of the real system. This is because the surface concentrations will be dependent on both temperature and time. The change in concentration of oxygen is also positive where it should be negative. By modeling change in surface concentrations, this will be improved.



### Iteration 3: Transient Conductive Heat Transfer

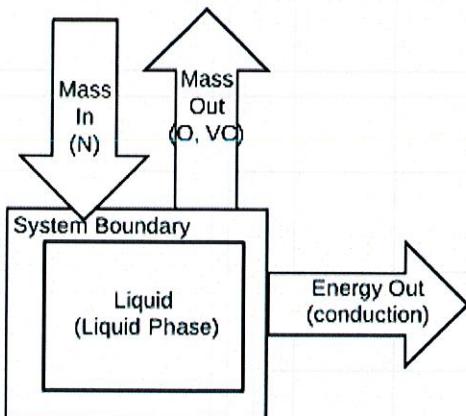
#### *Assumption Addressed*

- There is no preheat step, thus no heat transfer over the juice tank.

In this iteration, an initial and surface temperature of the liquid is input and transient heat transfer is modeled. The Henry's Law constants can then be modeled with the change in temperature to adjust the concentration values

#### *Simplifying Assumptions*

- Assumption 1: Conduction through the liquid is the limiting factor of heat transfer.
  - This means that conduction through the tank walls provide negligible resistance.
- Assumption 2: Conduction occurs around the horizontal surface area of the tank.
  - In reality, there will be some convection along the top of the tank as well.

**Diagram****Total Energy Balance**

For heat transfer, the total energy balance is defined as

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{Q}{\rho c}$$

In the system, there is no heat generation and no conduction into the system, so

$$\begin{aligned} E_{\text{out}} &= E_{\text{acc}} \\ \frac{\partial T}{\partial t} &= \alpha \frac{\partial^2 T}{\partial x^2} \end{aligned}$$

This is analogous to the diffusive mass transfer in iteration 2. Thus the temperature of the tank can be modeled as

$$T(x, t) = \frac{4}{\pi} \cos\left(\pi \cdot \frac{x}{2r}\right) \cdot e^{-\alpha \cdot \left(\frac{\pi}{2r}\right)^2 \cdot t} \cdot (T_i - T_s) + T_s$$

And the average temperature over time can be defined as

$$T_{\text{avg}}(t) = \int_0^r \frac{1}{r} \cdot T(x, t) dx$$

Where  $r$  is the characteristic length and  $\alpha = \frac{k}{\rho c}$ .

**Mixture and Gas Equilibrium**

The concentration of aqueous and gaseous solutions phase equilibrium is dependent on the chemical potential and partial pressure of the system. Gibb's free energy can be defined as

$$dG = -SdT + VdP$$

Where  $S$  is entropy,  $T$  is temperature,  $V$  is volume, and pressure is  $P$ . A simplifying assumption for this derivation is that the component being analyzed is an ideal, pure substance. Thus,

$$d\mu = dG$$

Where  $\mu$  is the chemical potential. Upon integration and application of the ideal gas law, the equation becomes

$$\mu = \mu^\circ + RT \ln(P/P^\circ)$$

Where  $\mu^\circ$  and  $P^\circ$  are a reference point. Since the components are not ideal, the pressures in the equation can then be replaced with fugacity  $f$ . The ratio between the reference fugacity and the fugacity

at a specific temperature and pressure can be defined as Henry's constant. Upon rearranging, the equation becomes

$$\mu - \mu^o = RT \ln(f/H)$$

If H is dependent on T, then a new equation can be derived.

$$H = H^o \exp\left(\frac{-\Delta h}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right)\right)$$

Where  $-\Delta h$  contains the chemical potential terms and  $-\Delta h/R$  is a constant depending on the gas.

In the model, the total pressure is determined with the same vapor equilibrium, but the concentration of oxygen and nitrogen at the surface becomes

$$K_N(t) := 6.5 \cdot 10^{-4} \cdot e^{-1300 \cdot \left( \frac{-1}{293.15} + \frac{1}{T_{avg}(t)+273} \right)} \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

$$K_O(t) := 1.3 \cdot 10^{-3} \cdot e^{-1700 \cdot \left( \frac{-1}{293.15} + \frac{1}{T_{avg}(t)+273} \right)} \frac{\text{mol}}{\text{L} \cdot \text{atm}}$$

$$C_{N_s}(t) := K_N(t) \cdot P_N \frac{\text{mol}}{\text{L}}$$

$$C_{O_s}(t) := K_O(t) \cdot P_O \frac{\text{mol}}{\text{L}}$$

This new condition is then applied to the mass diffusion equation in iteration 2. Below is an example of the input parameters and the given output.

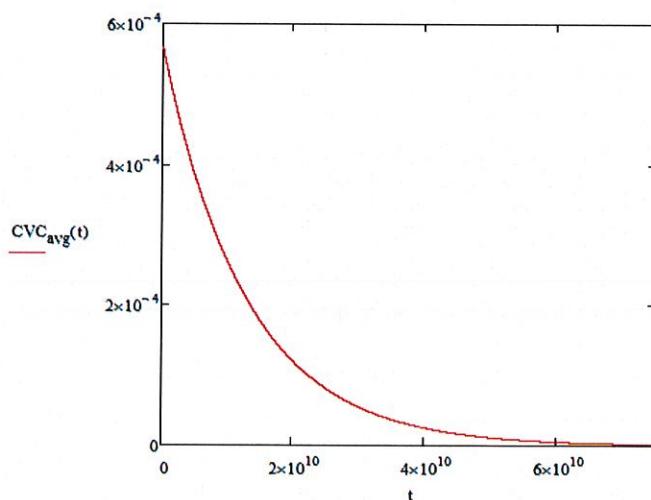
### ***Input Parameters***

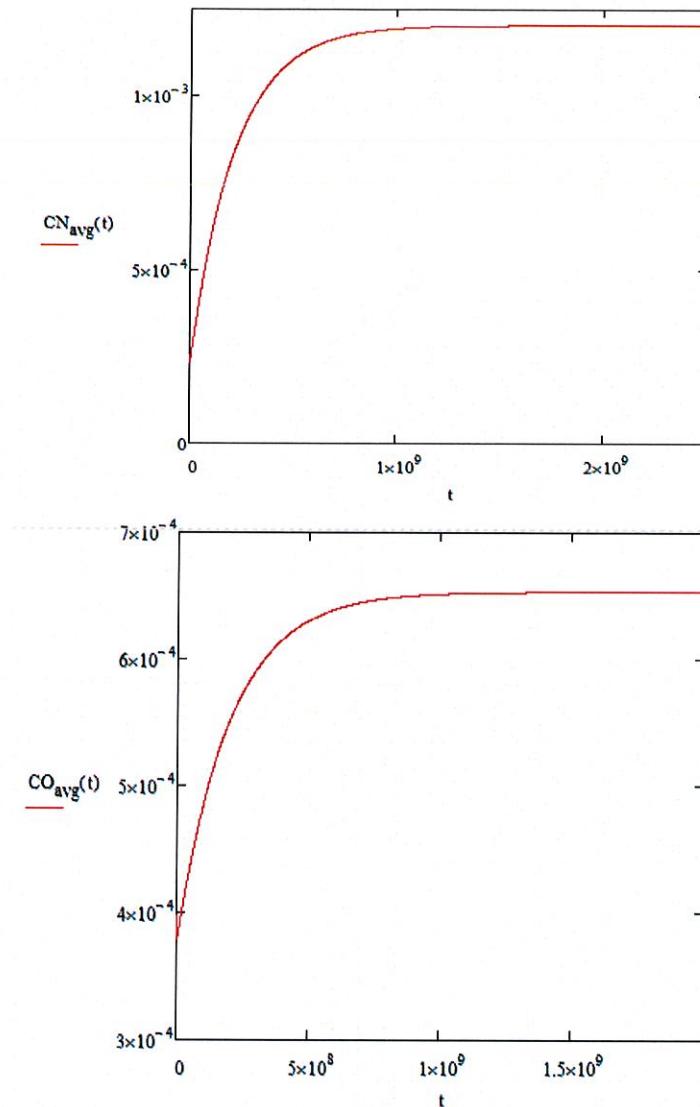
$$X_{A_N} = .78 \%$$

$$X_{A_O} = .21 \% \quad CVC_i = 7 \cdot 10^{-4} \frac{\text{kg}}{\text{L}} \quad CN_i = 0$$

$$X_{A_{vapor}} = .01 \% \quad V = 500 \text{ L} \quad CO_i = 3.125 \cdot 10^{-4} \quad L = 100 \text{ cm}$$

### ***Output***





Though the heat dependence did not have a massive effect on the trend of the plots, the concentrations of nitrogen and oxygen did approach the surface conditions more rapidly at elevated temperatures.

#### Iteration 4: Nitrogen Mass Flow

##### *Assumption Addressed*

*The headspace is at steady state.*

In order for deaeration to be a driving force for oxygen removal, a large quantity of nitrogen must be introduced to the system. Under the continued assumption that nitrogen is introduced into the headspace, the change in headspace composition over time can be modeled.

*The vapor pressures of water and the volatile compounds are constant over temperature.*

Saturated vapor pressure is dependent on temperature.

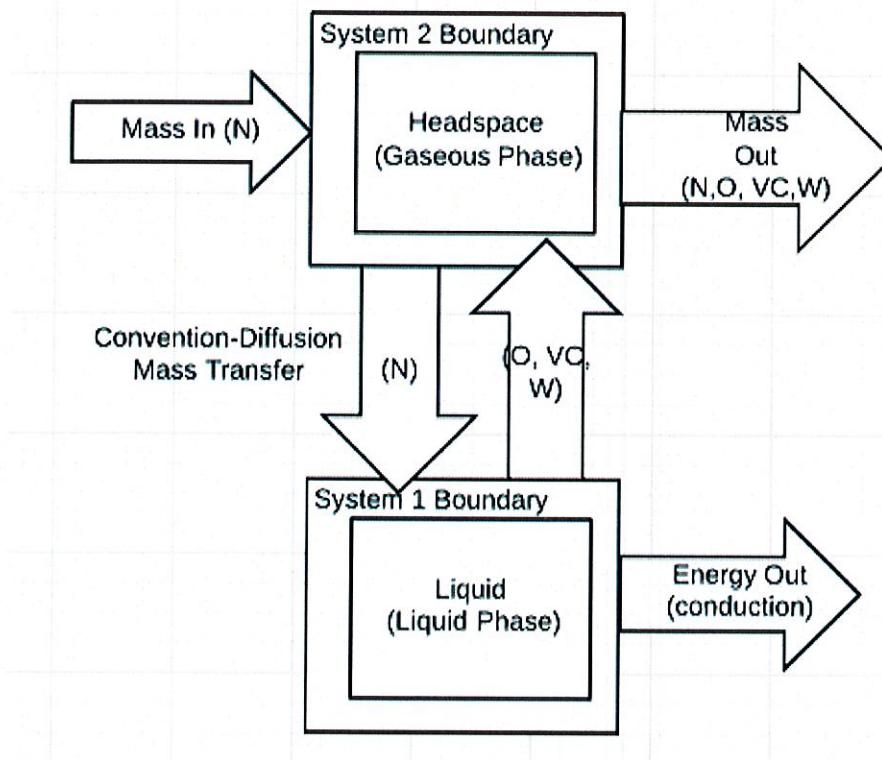
*Evaporation of volatile compounds and water is dependent on diffusion through the tank.*

For this iteration, the rate of evaporation will be determined by convection-diffusion through the headspace.

### Simplifying Assumptions

- Assumption 1: All gases and vapors in the system behave ideally.
- Assumption 2: Moles are conserved, but mass is not necessarily conserved.

### Diagram



### Headspace Mass Balance

Since the headspace is in a gaseous phase, there may be accumulation in the headspace. However, if there is a set pressure and volume, and the gases are ideal, then the number of moles in the headspace can be determined through volumetric flow rates.

As previously determined, the mass balance in the headspace is defined by this equation.

$$M_{in} - M_{out} = 0$$

Instead of mass, mole flow rates are now being used.

$$m_{in} - m_{out} = 0$$

### Headspace Component Molar Balance

Nitrogen:

$$m_{N,in} + m_{N,diff} - m_{N,out} = \frac{d}{dt} m_{N,H}$$

Oxygen:

$$m_{O,diff} - m_{O,out} = \frac{d}{dt} m_{O,H}$$

Volatile Compounds:

$$m_{VC,diff} - m_{VC,out} = \frac{d}{dt} m_{VC,H}$$

### Liquid Mass Balance

Nitrogen:

$$m_{N,diff} = \frac{d}{dt} m_{N,L}$$

Oxygen:

$$m_{O,diff} = \frac{d}{dt} m_{O,L}$$

Volatile Compounds:

$$m_{VC,diff} = \frac{d}{dt} m_{VC,L}$$

### **Convection Diffusion**

To determine the convection diffusion rates, a mass transfer coefficient was derived from the dimensionless Reynold numbers and Schmidt numbers. The derivation is shown below.

$$Re := \frac{D \cdot V_{in} \cdot 10^{-3}}{1.76 \cdot 10^{-5}} = 113.636$$

$$Sc_N := 280$$

$$Sc_O := 400$$

$$Sc_W := 340$$

$$Sc_{VC} := 500$$

Assuming Laminar Flow

$$h_N := \frac{D_N}{D} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_N^{-\frac{1}{3}} \right) = 4.075$$

$$h_O := \frac{D_O}{D} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_O^{-\frac{1}{3}} \right) = 4.589$$

$$h_{VC} := \frac{D_{VC}}{D} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_{VC}^{-\frac{1}{3}} \right) = 2.809$$

$$h_W := \frac{D_W}{D} \left( 0.664 \cdot Re^{\frac{1}{2}} \cdot Sc_W^{-\frac{1}{3}} \right) = 6.966$$

The equation for transfer then became

$$\frac{dm}{dt} = hA(C_s - CH)$$

Where A is the surface area, Cs is the surface concentration, and CH is the headspace concentration. The differential equations become

$$\begin{aligned}
 \text{CNL}'(t) &= \frac{-h_N \cdot \pi \cdot \left(\frac{D}{2}\right)^2}{V_L} \left[ \frac{\text{CNL}(t)}{K_N(t) \cdot 0.08206 \cdot (T_{\text{avg}}(t) + 273)} - \text{CNH}(t) \right] \\
 \text{COL}'(t) &= \frac{-h_O \cdot \pi \cdot \left(\frac{D}{2}\right)^2}{V_L} \left[ \frac{\text{COL}(t)}{K_O(t) \cdot 0.08206 \cdot (T_{\text{avg}}(t) + 273)} - \text{COH}(t) \right] \\
 \text{CVCL}'(t) &= \frac{-h_{VC} \cdot \pi \cdot \left(\frac{D}{2}\right)^2}{V_L} \left[ SVP_{VC}(t) \cdot \frac{\text{CVCL}(t)}{\text{CVCL}(t) + \text{CWL}(t)} \cdot \frac{1}{0.08206 \cdot (T_{\text{avg}}(t) + 273)} - \text{CVCH}(t) \right] \\
 \text{CWL}'(t) &= \frac{-h_W \cdot \pi \cdot \left(\frac{D}{2}\right)^2}{V_L} \left[ SVP_W(t) \cdot \frac{\text{CWL}(t)}{\text{CVCL}(t) + \text{CWL}(t)} \cdot \frac{1}{0.08206 \cdot (T_{\text{avg}}(t) + 273)} - \text{CWH}(t) \right] \\
 \text{CNH}'(t) &= \frac{V_{in}}{V_H} \cdot \frac{P_{\text{total}}}{0.08206 \cdot (T_{\text{avg}}(t) + 273)} + \frac{-V_L}{V_H} \cdot \text{CNL}'(t) - \frac{V_{in}}{V_H} \text{CNH}(t) \\
 \text{COH}'(t) &= \frac{-V_L}{V_H} \cdot \text{COL}'(t) - \frac{V_{in}}{V_H} \text{COH}(t) \\
 \text{CVCH}'(t) &= \frac{-V_L}{V_H} \cdot \text{CVCL}'(t) - \frac{V_{in}}{V_H} \text{CVCH}(t) \\
 \text{CWH}'(t) &= \frac{-V_L}{V_H} \cdot \text{CWL}'(t) - \frac{V_{in}}{V_H} \text{CWH}(t)
 \end{aligned}$$

With initial conditions

$$\text{CNL}(0) = \text{CN}_i$$

$$\text{COL}(0) = \text{CO}_i$$

$$\text{CVCL}(0) = M_{vci}$$

$$\text{CWL}(0) = M_w$$

$$CNH(0) = \frac{P_{NHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

$$COH(0) = \frac{P_{OHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

$$CVCH(0) = \frac{P_{VCHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

$$CWH(0) = \frac{P_{WHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

*Input Parameters*

$$T_s := 22$$

$$T_i := 32$$

$$XA_N := .78 \%$$

$$XA_O := .21 \%$$

$$XA_W := .01 \%$$

$$XA_{VC} := 0$$

$$CVC_i := 7 \cdot 10^{-4} \frac{\text{kg}}{\text{L}}$$

$$CW_i := 1 \frac{\text{kg}}{\text{L}}$$

$$CN_i := 180 \cdot 10^{-6}$$

$$CO_i := 180 \cdot 10^{-6}$$

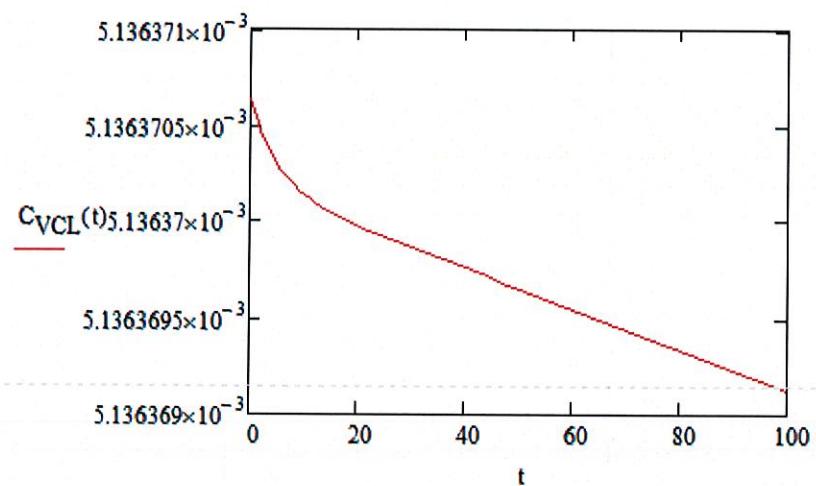
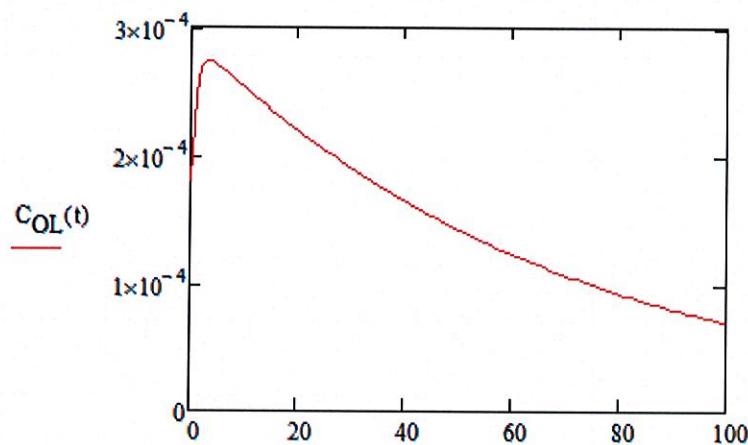
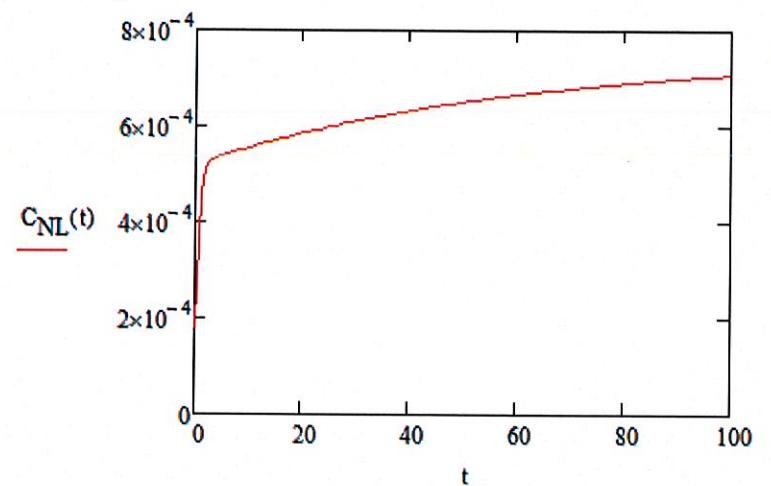
Volumes

$$V_{in} := 1 \frac{\text{L}}{\text{s}}$$

$$V_H := 50 \text{ L}$$

$$V_L := 500 \text{ L}$$

$$D := 2 \text{ m}$$

***System Output***

Where concentration is in mol/L of juice and  $t$  is in seconds. These more closely follow the expected trends. The increasing, then decreasing oxygen concentration in the juice is as expected with the

increasing nitrogen concentration in the headspace. There is also a very clear decrease in the molar concentration of volatile compounds, especially in the beginning when there is a higher driving force, which is also expected.

### Iteration 5: Ascorbic Acid Decomposition

#### *Assumption Addressed*

*No chemical reactions or energy transfers are occurring over deaeration.*

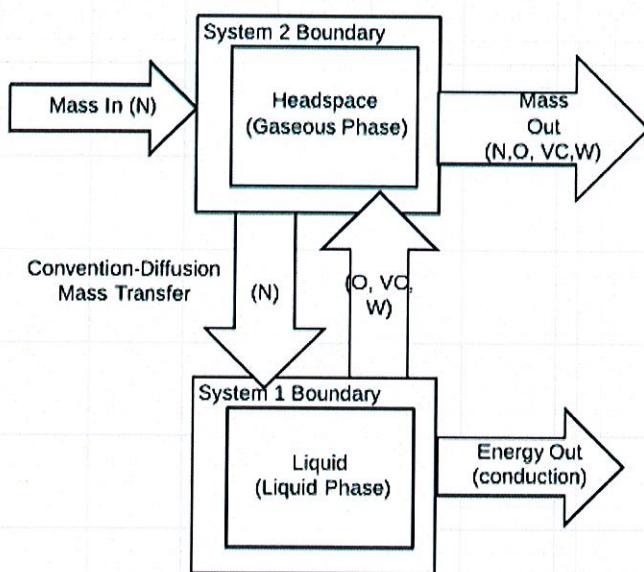
In the real system, ascorbic acid reacts with oxygen to decompose over time.

*There are no solvents or ash in the juice.*

The solid mass of the solution must be accounted for to determine accurate saturated vapor pressure.

#### *Diagram*

Same as Iteration 4, but a reaction is added in the juice



#### *Simplifying Assumptions*

- Assumption 1: The saturated vapor pressure of ascorbic acid is  $1.22 \times 10^{-13}$ , thus the diffusion at the surface is negligible (Ascorbic Acid, n.d.).
- Assumption 2: Juice is composed of the following constituents which have the following approximate molecular weights based on their most common component in parentheses.

Component	Molecular Weight (g/mol)
Soluble Solids	342.30 (Sucrose)
Ash	39.10 (Potassium)
Volatile Compounds	136.28 (Limonene)
Water	18.015 ( $\text{H}_2\text{O}$ )

- Assumption 3: the extent of reaction for the degradation of ascorbic acid is 1.

### Liquid Mass Balance

Nitrogen:

$$m_{N,diff} = \frac{d}{dt} m_{N,L}$$

Oxygen:

$$m_{O,diff} - m_{O,con} = \frac{d}{dt} m_{O,L}$$

Volatile Compounds:

$$m_{VC,diff} = \frac{d}{dt} m_{VC,L}$$

Ascorbic Acid

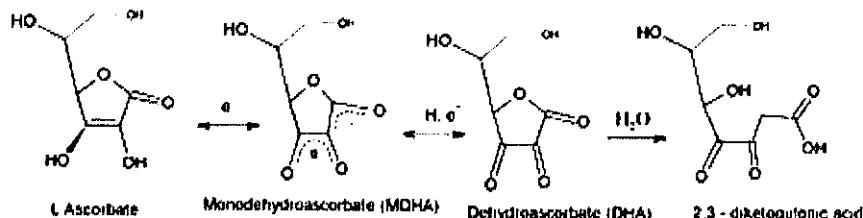
$$m_{AA,con} = \frac{d}{dt} m_{AA,L}$$

2,3-diketogulonic Acid

$$m_{DKG,gen} = \frac{d}{dt} m_{DKG,L}$$

In order to determine the rates of generation and consumption, the rate constant was found in literature (Garcia-Torres, et. al., 2009) and related to a non-elementary second order reaction. Thus, the reaction below became modeled as

$$\frac{dm}{dt} = k(mO)(mAA)$$



Thus the ordinary differential equations become

$$\begin{aligned} \text{CNL}'(t) &= \frac{-h_N \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ \frac{\text{CNL}(t)}{K_N(t) \cdot 0.08206 \cdot (T_{avg}(t) + 273)} - \text{CNH}(t) \right] \\ \text{COL}'(t) &= \frac{-h_O \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ \frac{\text{COL}(t)}{K_O(t) \cdot 0.08206 \cdot (T_{avg}(t) + 273)} - \text{COH}(t) \right] - K_1(t) \cdot \text{CAAL}(t) \cdot \text{COL}(t) \\ \text{CVCL}'(t) &= \frac{-h_{VC} \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ SVP_{VC}(t) \cdot \frac{\text{CVCL}(t) \cdot V_L}{\text{CVCL}(t) \cdot V_L + \text{CWL}(t) \cdot V_L + mol_{SS} + mol_A} \cdot \frac{1}{0.08206 \cdot (T_{avg}(t) + 273)} - \text{CVCH}(t) \right] \\ \text{CWL}'(t) &= \frac{-h_W \cdot \pi \cdot \left(\frac{D_T}{2}\right)^2}{V_L} \left[ SVP_W(t) \cdot \frac{\text{CWL}(t) \cdot V_L}{\text{CVCL}(t) \cdot V_L + \text{CWL}(t) \cdot V_L + mol_{SS} + mol_A} \cdot \frac{1}{0.08206 \cdot (T_{avg}(t) + 273)} - \text{CWH}(t) \right] \end{aligned}$$

$$\text{CAAL}'(t) = -2 K_1(t) \cdot \text{CAAL}(t) \cdot \text{COL}(t)$$

$$\text{CDKGL}'(t) = 2 K_1(t) \cdot \text{CAAL}(t) \cdot \text{COL}(t)$$

$$\text{CNH}'(t) = \frac{V_{in}}{V_H} \cdot \frac{P_{total}}{0.08206 \cdot (T_{avg}(t) + 273)} - \frac{V_L}{V_H} \cdot \text{CNL}'(t) - \frac{V_{in}}{V_H} \text{CNH}(t)$$

$$\text{COH}'(t) = \frac{-V_L}{V_H} \cdot \text{COL}'(t) - \frac{V_{in}}{V_H} \text{COH}(t)$$

$$\text{CVCH}'(t) = \frac{-V_L}{V_H} \cdot \text{CVCL}'(t) - \frac{V_{in}}{V_H} \text{CVCH}(t)$$

$$\text{CWH}'(t) = \frac{-V_L}{V_H} \cdot \text{CWL}'(t) - \frac{V_{in}}{V_H} \text{CWH}(t)$$

With initial conditions

$$\text{CNL}(0) = \text{CN}_i$$

$$\text{COL}(0) = \text{CO}_i$$

$$\text{CVCL}(0) = M_{vci}$$

$$\text{CWL}(0) = M_w$$

$$\text{CAAL}(0) = \text{CAA}_i$$

$$\text{CDKGL}(0) = 0$$

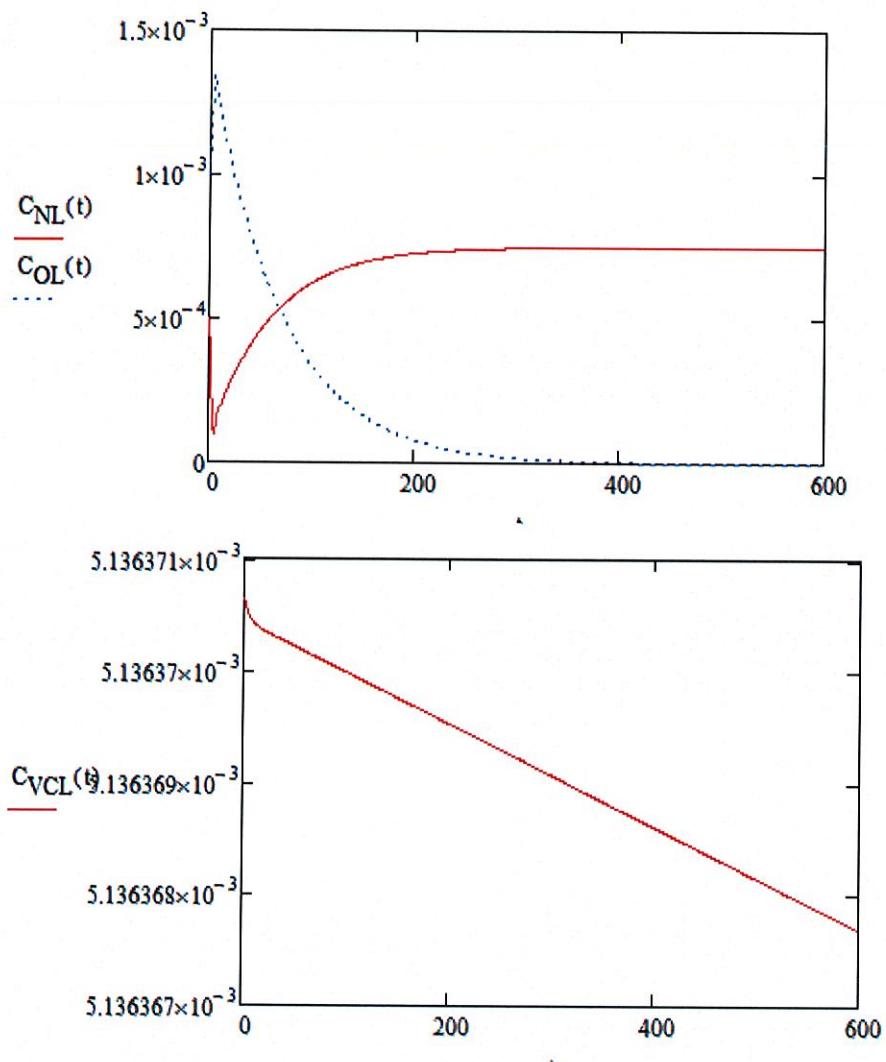
$$CNH(0) = \frac{P_{NHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

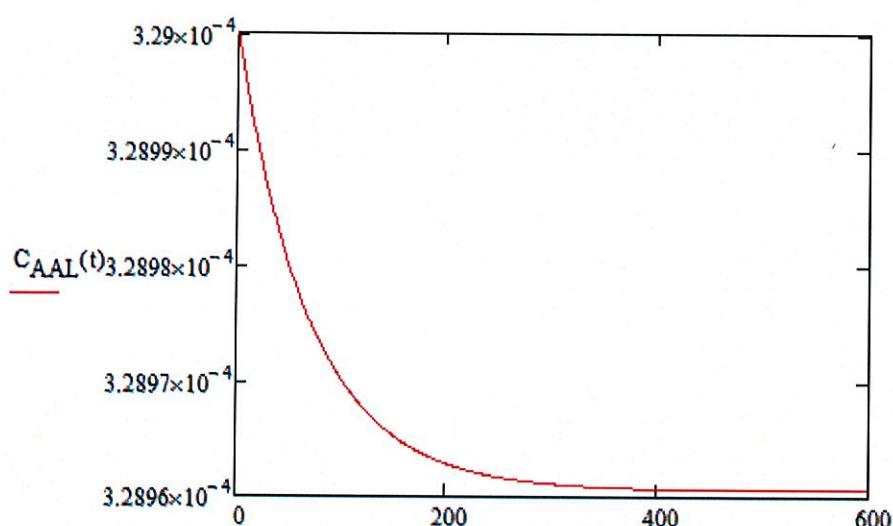
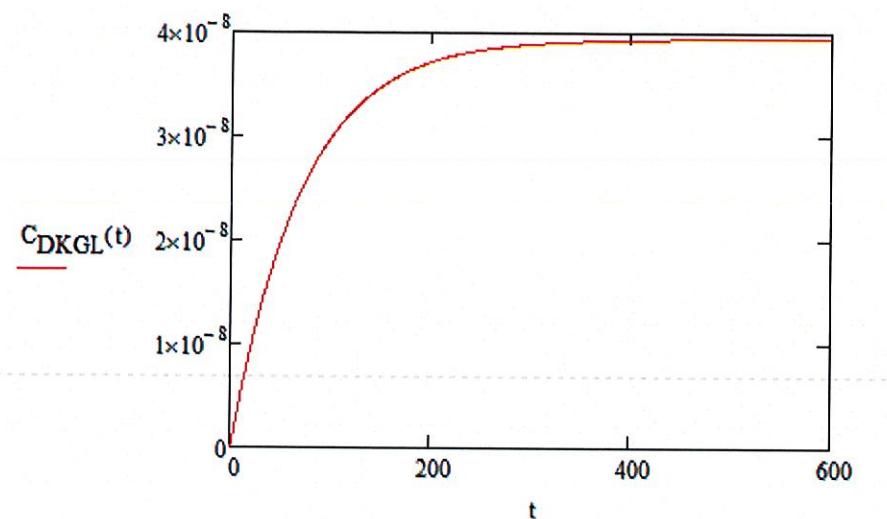
$$COH(0) = \frac{P_{OHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

$$CVCH(0) = \frac{P_{VCHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

$$CWH(0) = \frac{P_{WHi}}{[0.08206 \cdot (T_{avg}(0) + 273)]}$$

***Input Parameters*****USER INPUTS****Temperature Initial Conditions** $T_s := 22$  Input Surface Temperature of Tank ( $T_s$ ) $T_i := 32$  Input Initial Temperature of the Juice ( $T_i$ )**Initial Composition of Air In Headspace** $X_{A_N} := 0$  % Input Ratio of Nitrogen in the Air (Typically 0.78) $X_{A_O} := 99$  % Input Ratio of Oxygen in the Air (Typically 0.21) $RH := 10$  % Input Relative Humidity $P_{total} := 1$  atm Input Total Pressure in the Headspance**Initial Concentrations in Liquid** $CVC_i := 7 \cdot 10^{-4}$   $\frac{\text{kg}}{\text{L}}$  Input Initial Concentration of Volatile Compounds in Juice $CW_i := .888$   $\frac{\text{kg}}{\text{L}}$  Input Initial Concentration of Water in Juice $CAA_i := 3.29 \cdot 10^{-4}$   $\frac{\text{kg}}{\text{L}}$  Input Initial Concentration of Ascorbic Acid in Juice $CSS_i := .118$   $\frac{\text{kg}}{\text{L}}$  Input Concentration of Soluble Solids in Juice $CA_i := 3.0$   $\frac{\text{kg}}{\text{L}}$  Input Concentration of Ash in Juice $CN_i := 5 \cdot 10^{-4}$   $\frac{\text{mol}}{\text{L}}$  $CO_i := 10 \cdot 10^{-4}$   $\frac{\text{mol}}{\text{L}}$  $pH := 4$  Input the pH of the Juice**Tank Volumes** $V_H := 50$  L Input Total Air Volume in the Headspace $V_L := 500$  L Input Total Juice Volume $D_T := 2$  m Input Diameter of Tank $V_{in} := 1$   $\frac{\text{L}}{\text{s}}$  Input Volumetric Flow Rate of Nitrogen in Headspace

**System Output**



This model follows all expected trends for the system and is used as the final iteration.

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