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UNIVERSIDAD TECNICA FEDERICO SANTA MARIA

MODELING HEAD SPACE PRESSURE BUILD UP AS A POLYTROPIC PROCESS IN RETORT STERILIZATION OF CANNED FOODS

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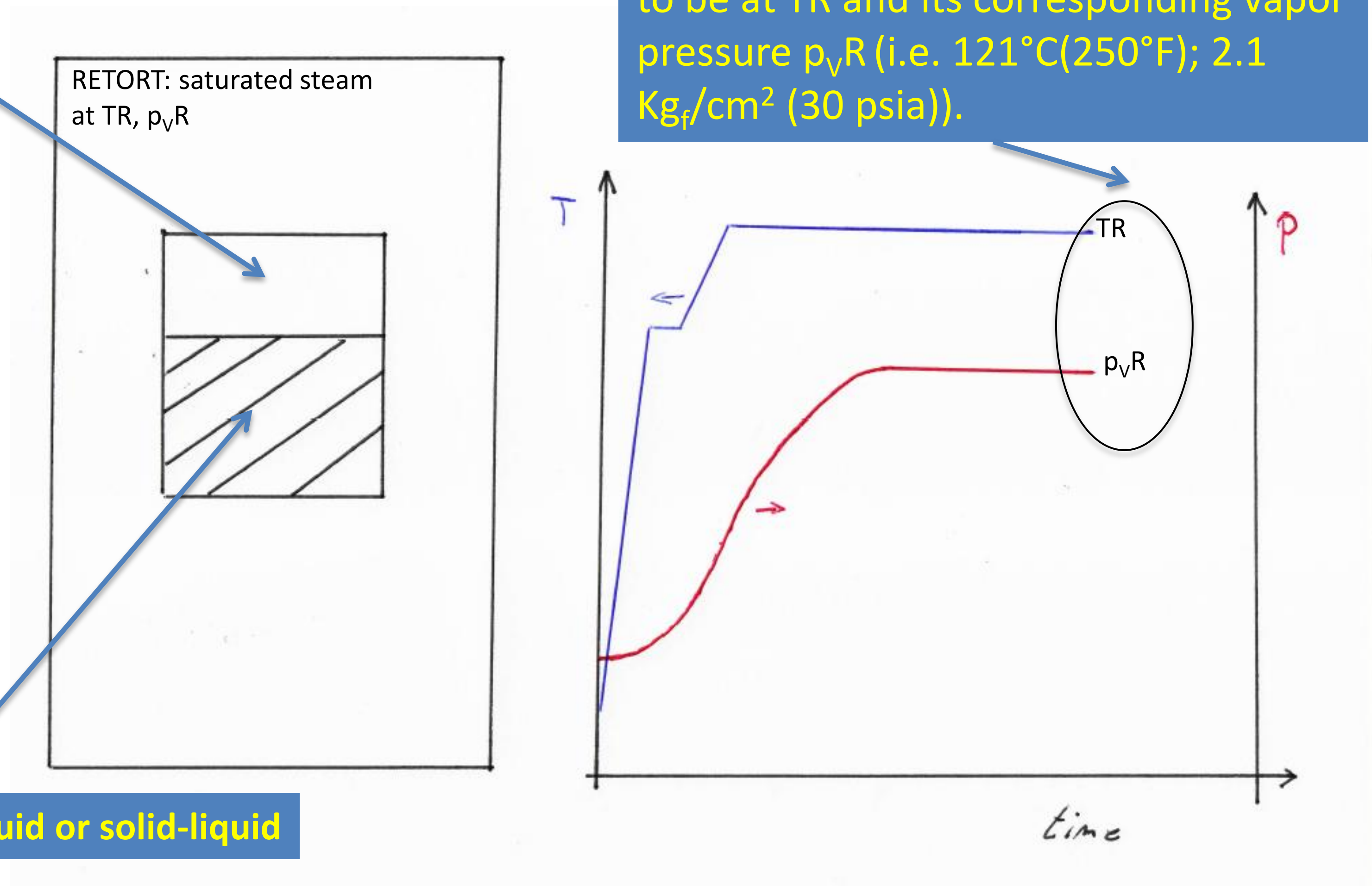
Introduction
(What is going on with head space pressure?)

HEAD-SPACE: water-vapor, air or other gases

At equilibrium: the RETORT is going to be at TR and its corresponding vapor pressure p_VR (i.e. 121°C(250°F); 2.1 Kg_f/cm^2 (30 psia)).



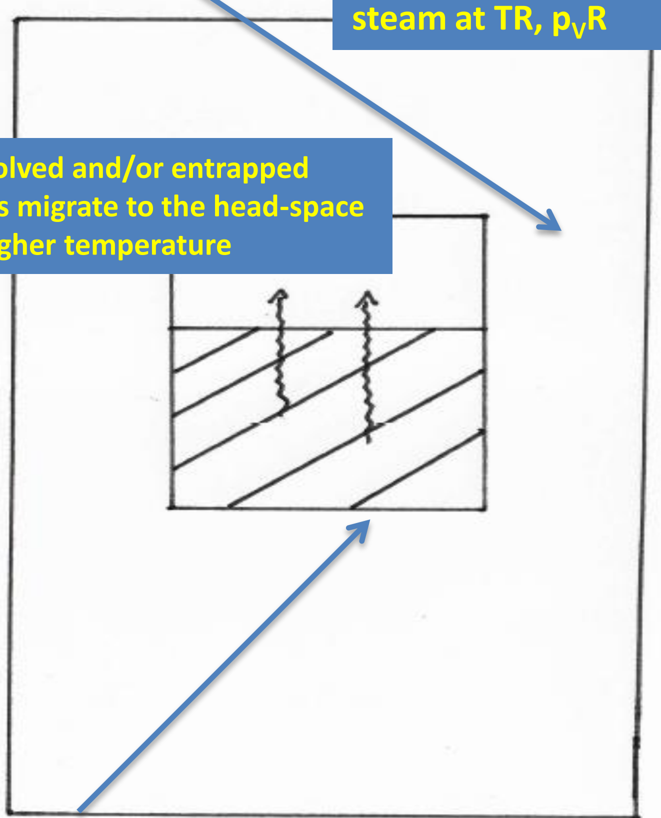
FOOD: solid, liquid or solid-liquid

Why Does it Happen?

HEAD-SPACE: water vapor + air or other gases

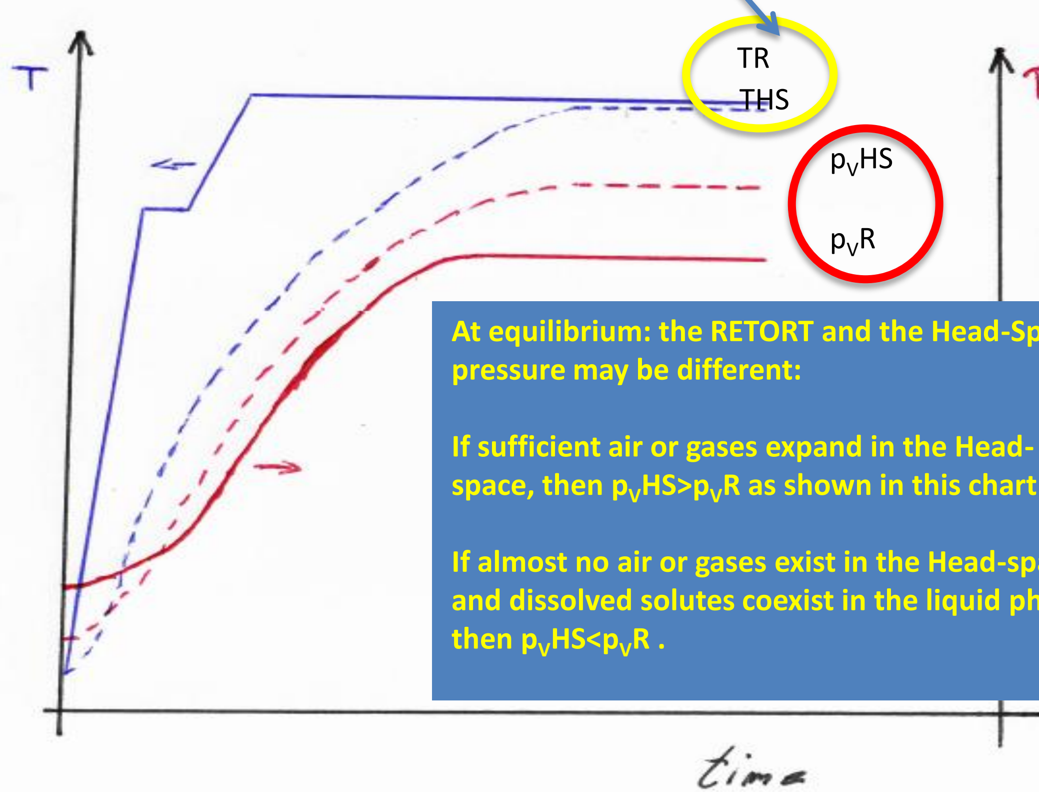
RETORT: saturated steam at TR, $p_V R$

Dissolved and/or entrapped gases migrate to the head-space at higher temperature



FOOD: solid, liquid or solid-liquid

At equilibrium: the RETORT and the Head-Space temperature equalizes (i.e. 121°C / 250°F).

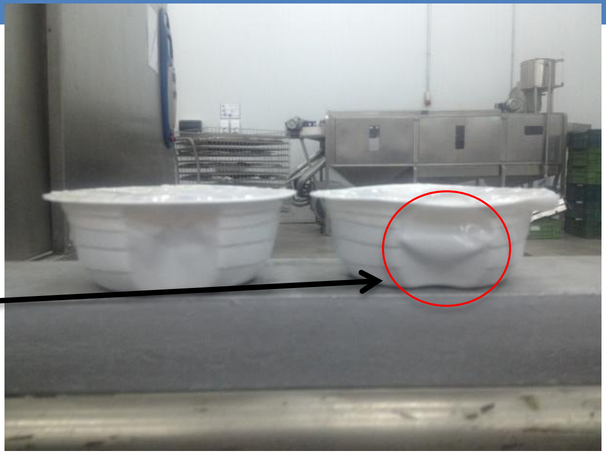


At equilibrium: the RETORT and the Head-Space pressure may be different:

If sufficient air or gases expand in the Head-space, then $p_V HS > p_V R$ as shown in this chart.

If almost no air or gases exist in the Head-space, and dissolved solutes coexist in the liquid phase, then $p_V HS < p_V R$.

What Are the Consequences?

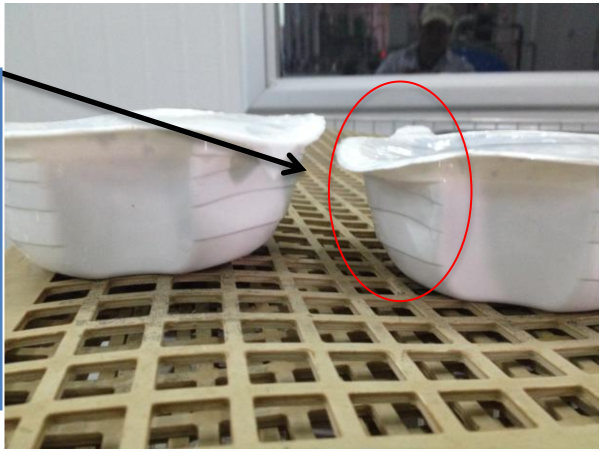


At equilibrium: the RETORT and the Head-Space pressure may be different:

If sufficient air or gases expand in the Head-space, then $p_V HS > p_V R$.

If almost no air or gases exist in the Head-space, and dissolved solutes coexist in the liquid phase, then $pVHS < p_V R$.

As a result, seaming stress and deformation can occur, and <u>controlled over-riding air pressure profile is required</u>



Common practice in industry is to determine these required pressure-profiles of overriding air pressure by trial and error, or real-time on-line detecting devices, both of which are costly.

Most Recent Mathematical Model

The most recent model by Ghai and others (2011) utilized the mathematical equation for an ideal gas undergoing a reversible adiabatic process at constant volume expressed by the equation of state for an ideal gas which takes into account the Adiabatic Index or Isentropic Expansion Factor, *γ*.

$$P_1^{\gamma-1} / \ T_1^{\gamma} = P_2^{\gamma-1} / \ T_2^{\gamma}$$

where $P\,V^{\gamma}$ and $P^{\gamma-1}\,T^{-\gamma}$ are constant.

and *γ* is the Heat Capacity Ratio; $\gamma = Cp / Cv = (\alpha + 1) / \alpha$

***α* is the number of degrees of freedom divided by 2 (3/2 for monatomic gas, 5/2 for diatomic gas.**

However, they admitted that the thermal process was neither adiabatic nor isentropic. Entropy had to be transferred from the retort heating medium to the module. Therefore, their approach was only a first approximation.

Hypothesis of This Work

- **Assume head space pressure build up to be a thermodynamically imprecise "polytropic" process.**

- **In this case, the isentropic expansion factor, *γ*, would need to be replaced by an alternative polytropic factor (β) that could take into account the combined effects of various initial and boundary conditions of temperature, pressure, head space volume and solute (salt) concentration.**

Objectives

- Estimate the numerical value for the polytropic factor (β).
- Develop a new mathematical model incorporating the polytropic factor, β, in place of the isentropic expansion factor, *γ*, used in previous models.
- Execute a design of laboratory experiments that would measure the actual head space pressures under a predetermined range of initial and boundary conditions of temperature, pressure, head space volume and salt concentration.
- Validate the new model by comparing model predicted with experimentally measured head space pressures under the various initial and boundary conditions tested in the study.

Model Development

A general expression for the internal pressure within the head space would be:

$$P_{head\ space} = P_{vsat}\,(RH) + P_{air}$$

Where: P_{vsat} is partial pressure of saturated vapor, RH is relative humidity, and P_{air} is partial pressure of air.
The partial pressure of air was estimated from the ideal gas law modified to incorporate the polytropic expansion factor (β), assuming the number of moles and volume of air remain constant throughout the process.   Thus, the final partial pressure of air at any final temperature could be expressed as follows:

$$P_f^{\,air} = P_i^{\,air}\,(T_f / T_i)^{\beta}$$

Where P_i^{air} is initial partial pressure of air, and T_f and T_i are final and initial temperatures, respectively. Initial partial pressure of air was determined by subtracting the initial vapor partial pressure adjusted for relative humidity from the total initial head space pressure:

$$P_i^{\,air} = P_i^{\,head\ space} - P_{vsat(Ti)}\,(RH)$$

Model Development

The partial pressure of saturated vapor from the solution was estimated from the equation of Maxwell Boltzman for probabilistic distribution, expressed as:

$$P_v = \alpha RT \left[e^{-(H/RT + X_2)} \right]$$

Where X_2 is the mole fraction of the solute in the solution, H is enthalpy at temperature (T), R is universal gas constant, and αRT could be replaced by the vapor pressure at a reference temperature, $P_{v(Tref)}$, leading to an expression for the vapor pressure as a function of temperature and mole fraction of solute:

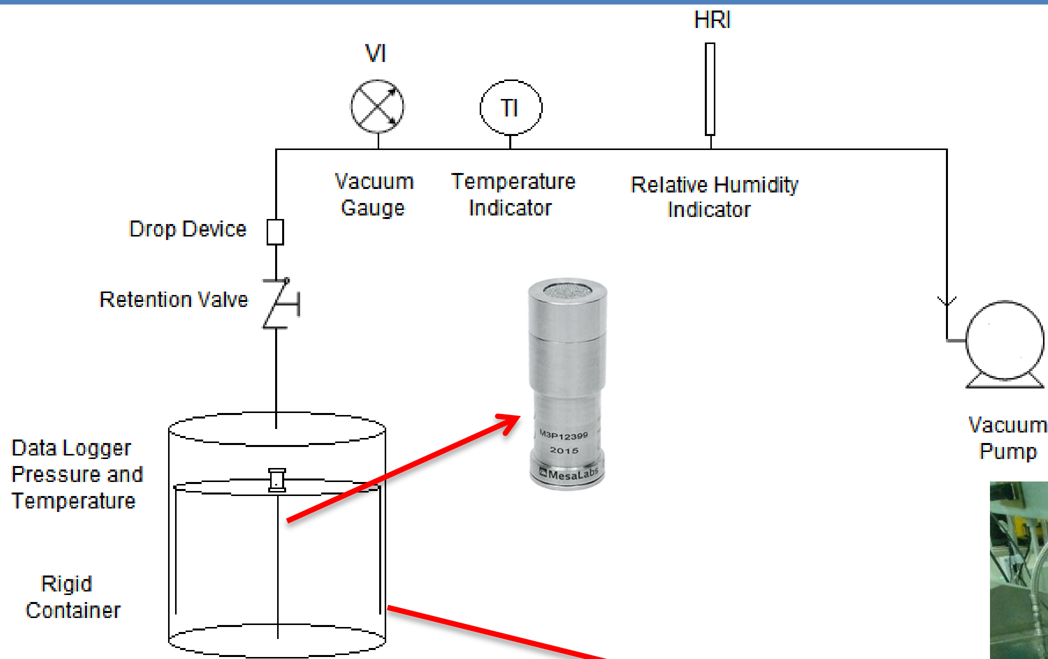
$$P_{v\ solution} = P_{v\ (Tref)} \left[e^{-\Delta Hvap/R\ (1/\ Tf - 1/Tref) - X_{solute}} \right]$$

Summing the expressions for *Pv solution* and P_f^{air} will give the complete mathematical expression for the new model:

$$P_{head\ space} = P_{v\ (Tref)} \left[e^{-\Delta Hvap/R\ (1/\ Tf - 1/Tref) - X_{solute}} \right] + P_i^{air} \left(T_f / T_i\right)^{\beta}$$

At this point, effective execution of the model would rely on finding the correct numerical value for the polytropic expansion factor (β). This was accomplished by executing the model with judiciously chosen values of (β) for a given set of initial and boundary conditions chosen from the midpoint within the design of experiments, and comparing results predicted by the model with experimental results.

Materials and Methods



A thick rigid pressure vessel in the size and shape of a cylindrical food can with internal volume of 550 mL was fabricated.

Internal temperatures and pressures were measured with wireless data loggers (Mesa Lab M3P1 12399)

Factorial Design of Experiments

P° inicial [psia] (A)	Vol. headspace (B)	T° final [°C] (C)	%*NaCl* (D)	NIVEL
6,5	50 ml	116	0%	-1
10,5	225 ml	121	2,5%	0
14,5	400 ml	126	5%	+1

X_1	X_2	X_3	X_4
-1	-1	0	0
1	-1	0	0
-1	1	0	0
1	1	0	0
0	0	-1	-1
0	0	1	-1
0	0	-1	1
0	0	1	1
0	**0**	**0**	**0**
-1	0	0	-1
1	0	0	-1
-1	0	0	1
1	0	0	1
0	-1	-1	0
0	1	-1	0
0	-1	1	0
0	1	1	0
0	**0**	**0**	**0**
0	-1	0	-1
0	1	0	-1
0	-1	0	1
0	1	0	1
-1	0	-1	0
1	0	-1	0
-1	0	1	0
1	0	1	0
0	**0**	**0**	**0**

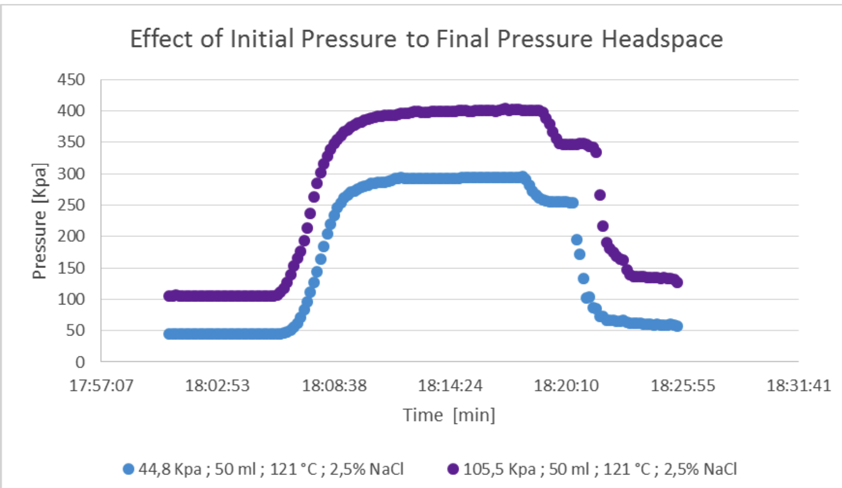
Results from Executing Design of Experiments

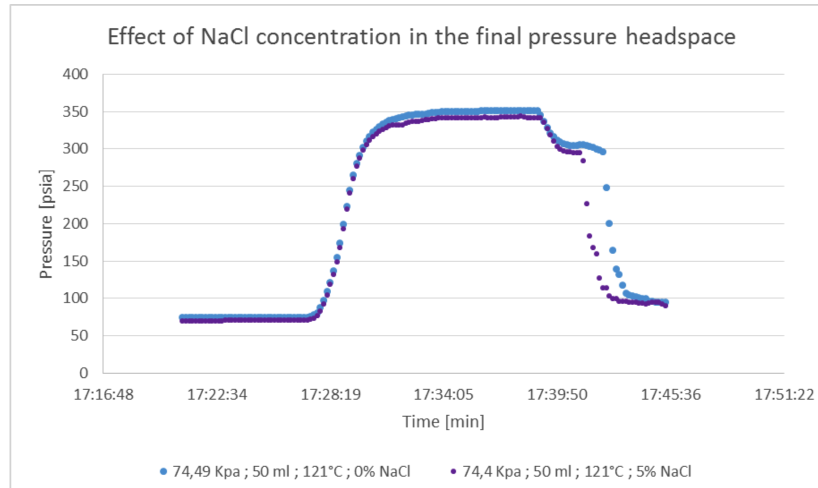
Results (measured final head space pressure) from each of the 27 experiments that were carried out in accordance with the design of experiments are summarized in the following Table

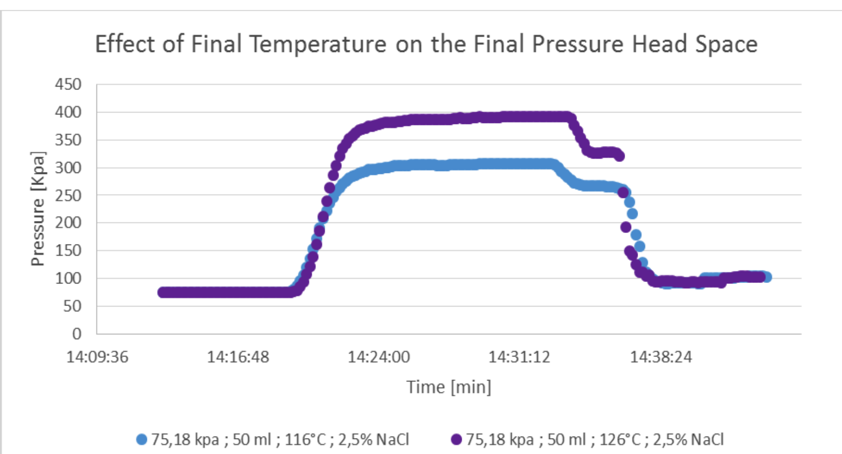
Exp.	Pi [psia]	Vi [mL]	Tf °C	%Sal	Pi	Vi	Tf	% Sal	P final [psia]
1	6,5	50	121	2,5	-1	-1	0	0	42,06
2	14,5	50	121	2,5	1	-1	0	0	57,37
3	6,5	400	121	2,5	-1	1	0	0	38
4	14,5	400	121	2,5	1	1	0	0	50,17
5	10,5	225	116	0	0	0	-1	-1	39,45
6	10,5	225	126	0	0	0	1	-1	50,36
7	10,5	225	116	5	0	0	-1	1	39,88
8	10,5	225	126	5	0	0	1	1	50,35
9	**10,5**	**225**	**121**	**2,5**	**0**	**0**	**0**	**0**	45,47
10	6,5	225	121	0	-1	0	0	-1	38,39
11	14,5	225	121	0	1	0	0	-1	51,16
12	6,5	225	121	5	-1	0	0	1	39,26
13	14,5	225	121	5	1	0	0	1	49,14
14	10,5	50	116	2,5	0	-1	-1	0	43,96
15	10,5	400	116	2,5	0	1	-1	0	38,95
16	10,5	50	126	2,5	0	-1	1	0	56,04
17	10,5	400	126	2,5	0	1	1	0	49,91
18	**10,5**	**225**	**121**	**2,5**	**0**	**0**	**0**	**0**	45,74
19	10,5	50	121	0	0	-1	0	-1	50,26
20	10,5	400	121	0	0	1	0	-1	44,81
21	10,5	50	121	5	0	-1	0	1	48,94
22	10,5	400	121	5	0	1	0	1	44,12
23	6,5	225	116	2,5	-1	0	-1	0	34,42
24	14,5	225	116	2,5	1	0	-1	0	46,44
25	6,5	225	126	2,5	-1	0	1	0	44,32
26	**14,5**	**225**	**126**	**2,5**	**1**	**0**	**1**	**0**	**57,08**
27	**10,5**	**225**	**121**	**2,5**	**0**	**0**	**0**	**0**	**45,6**

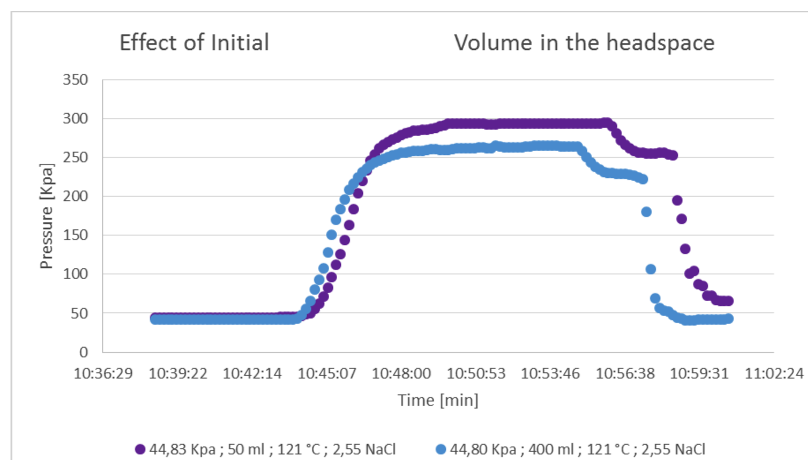
Graphical Experimental Results

(ΔPi=6.5-15.3psi, ΔNaCl=0-5%, ΔTr=116-126^{0}C, ΔVi=50-400ml)









Analysis of Experimental Results

Careful review of these results has revealed the following observations, some of which were to be intuitively expected:

- **Increase in initial temperature had no effect on final head space pressure.**
- **Increase in initial pressure expectedly increased final head space pressure.**
- **Increased salt concentration reduced final head space pressure.**
- **Increased retort temperature expectedly increased final head space pressure.**
- **Reduced head space volume surprisingly led to increased final head space pressure.**

Further Analysis of Experimental Results

Head Space Volume Related to Polytropic Expansion Factor:

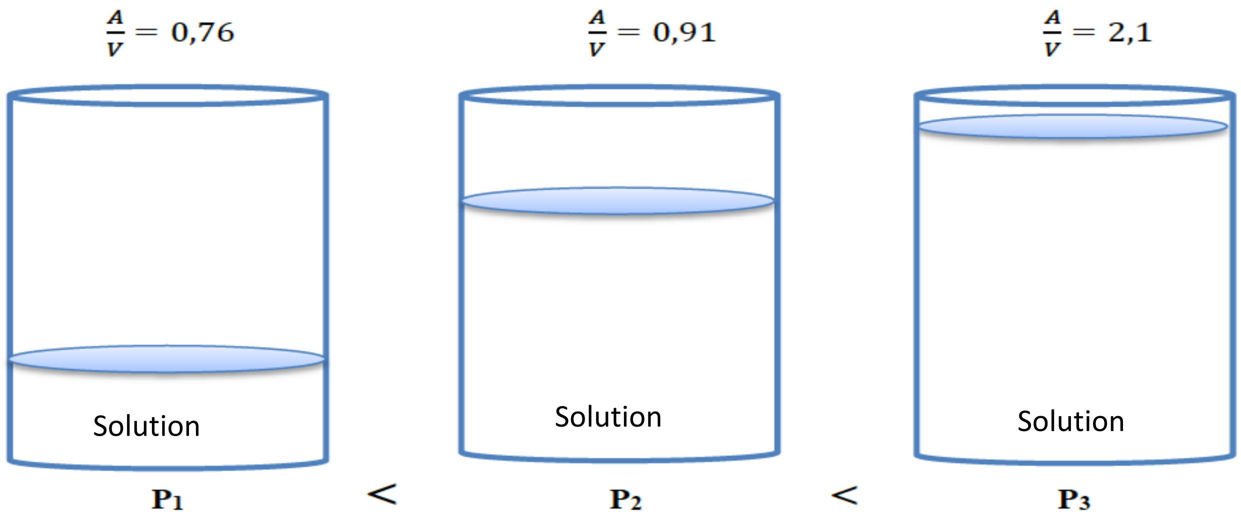
- **Head space volume may have a significant and surprising effect on final head space pressure.**
- **Increasing head space pressure with decreasing head space volume may be explained by noting that the surface area at the interface between liquid and head space remains the same regardless of head space volume within the cylindrical container.**
- **Therefore, ratio of surface area to volume changes dramatically with head space volume.**
- **Although there are fewer moles of air and vapor in the smaller head space, these fewer moles receive the same level of energy at retort temperature as those within larger head space volumes.**
- **Because of the short distances between liquid surface and top of the container in smaller head space volume, the same high level of kinetic energy delivered to these fewer moles causes far more molecular collisions with these surfaces than with larger head space volumes, thus, exerting greater pressure.**
- **This gave cause to revisit the equation of state for a polytropic expansion at constant volume that was presented earlier:**

$$P_f^{air} = P_i^{air} (T_f / T_i)^{\beta}$$

Area/Volume Ratio Related to β

- The polytropic coefficient, β, is the key factor to obtaining optimum model performance.

- β should be inversely proportional to head space volume, and could be estimated by comparing experimental results with those predicted by the model with different numerical values for β in search of that value resulting in least error squared for each of the three head space volumes tested in the design of experiments.



Determining Numerical Value for β

- The values of β that were found for each of the three head space volumes tested are shown below, along with the ratio of area to head space volume (A/V).
- Note that values found for β were in close proportion to values of A/V. Therefore, the greater the head space volume, the closer the expansion approaches an isentropic process.

Headspace	β	A/V	Head-Space final pressure
400 mL	1	0,76	$P_{v\,(T_{ref})} \cdot e^{-\frac{\Delta H_{vap}}{R}\cdot\left(\frac{1}{T_f}-\frac{1}{T_{ref}}\right)-X_{soluto}} + P_i^{aire} \cdot \left(\frac{T_f}{T_i}\right)$
225 mL	1,25	0,91	$P_{v\,(T_{ref})} \cdot e^{-\frac{\Delta H_{vap}}{R}\cdot\left(\frac{1}{T_f}-\frac{1}{T_{ref}}\right)-X_{soluto}} + P_i^{aire} \cdot \left(\frac{T_f}{T_i}\right)^{1{,}25}$
50 mL	2,2	2,1	$P_{v\,(T_{ref})} \cdot e^{-\frac{\Delta H_{vap}}{R}\cdot\left(\frac{1}{T_f}-\frac{1}{T_{ref}}\right)-X_{soluto}} + P_i^{aire} \cdot \left(\frac{T_f}{T_i}\right)^{2{,}2}$

Resulting Regression Model

$$P\,final = 45{,}6333 + 6{,}24167 \cdot Pi - 3{,}2 \cdot Vi + 4{,}05833 \cdot Tf - 0{,}25 \cdot Xnacl - 0{,}133333 \cdot Pi^2 - 0{,}775 \cdot Pi \cdot Vi + 0{,}2 \cdot Pi \cdot Tf - 0{,}75 \cdot Pi \cdot Xnacl + 1{,}25417 \cdot Vi^2 - 4{,}3 \cdot Vi \cdot Tf + 0{,}175 \cdot Vi \cdot Xnacl - 0{,}433333 \cdot Tf^2 - 0{,}125 \cdot Tf \cdot Xnacl - 0{,}345833 \cdot Xnacl^2$$

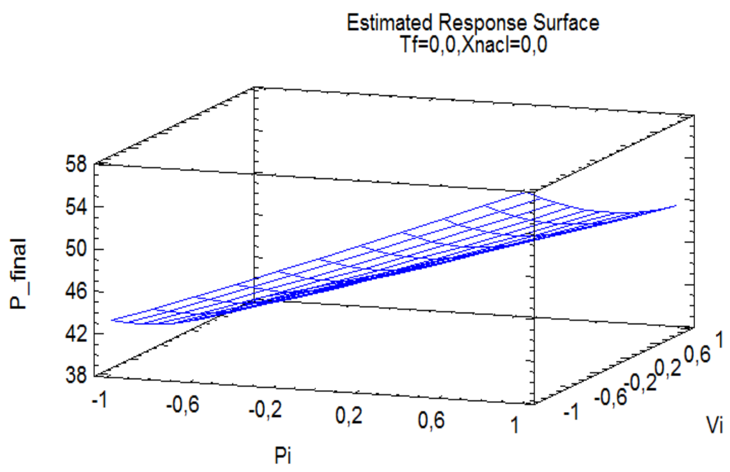
Analysis of Variance for P_final

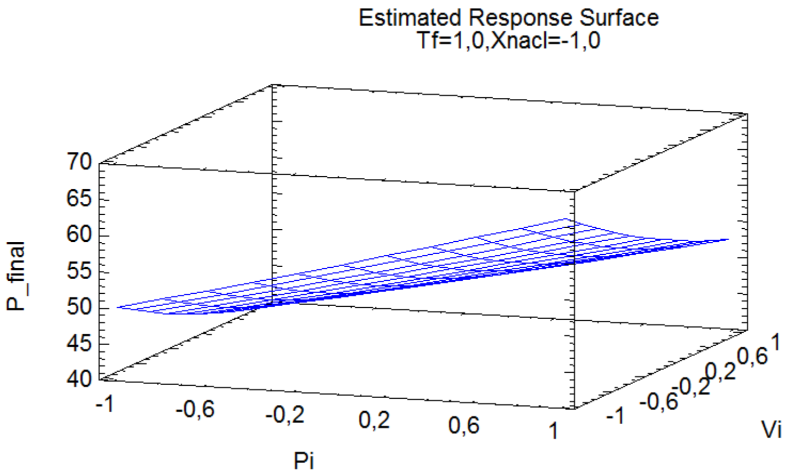
Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
A:Pi	499,23	1	499,23	287,56	0,0000
B:Vi	122,88	1	122,88	70,78	0,0000
C:Tf	308,053	1	308,053	177,44	0,0000
D:Xnacl	1,08	1	1,08	0,62	0,4486
AA	0,415648	1	0,415648	0,24	0,6352
AB	3,0625	1	3,0625	1,76	0,2136
AC	0,81	1	0,81	0,47	0,5101
AD	0,2025	1	0,2025	0,12	0,7398
BB	8,05787	1	8,05787	4,64	0,0566
BC	12,96	1	12,96	7,47	0,0211
BD	2,1025	1	2,1025	1,21	0,2969
CC	0,391204	1	0,391204	0,23	0,6452
CD	0,09	1	0,09	0,05	0,8245
DD	0,466759	1	0,466759	0,27	0,6154
blocks	1,92074	2	0,96037	0,55	0,5918
Total error	17,3609	10	1,73609		
Total (corr.)	982,567	26			

R-squared = 98,2331 percent
R-squared (adjusted for d.f.) = 96,1717 percent
Standard Error of Est. = 1,31761

$$P_{final} = 45.63 + 6.24(Pi) - 3.20(V_i) + 4.06(T_f) - 4.30(V_i \cdot T_f)$$

Response Surface Results





Tf: 121°C y Xnacl: 2,5%

Tf: 126°C y Xnacl: 0 %

Model Validation Results

Average Error:

Polytropic Model = 1.16%
Surface Response = 3.4%

Exp	Pi [psia]	Vi [ml]	Tf [°C]	% Sal	P Experimental [psia]	Polytropic Model [psia]	%Error
1	6,6	50	121,72	2,50%	42,06	42,37	0,74
2	15,5	50	122,02	2,50%	57,37	60,3	5,11
3	6,1	400	121,74	2,50%	38	38,21	0,55
4	15,1	400	121,52	2,50%	50,17	49,74	0,86
5	10,2	225	116,85	0%	39,45	40,21	1,93
6	10,5	225	126,85	0%	50,36	50,69	0,66
7	10,7	225	116,62	5%	39,88	40,27	0,98
8	10,9	225	126,55	5%	50,35	50,48	0,26
9	**11**	**225**	**121,61**	**2,50%**	**45,47**	**44,68**	1,74
10	6,3	225	121,76	0%	38,39	39,23	2,19
11	15,1	225	121,78	0%	51,16	51,58	0,82
12	6,3	225	121,74	5%	39,26	38,75	1,30
13	15,1	225	120,32	5%	49,14	49,98	1,71
14	10,9	50	116,82	2,50%	43,96	45,46	3,41
15	10,9	400	115,83	2,50%	38,95	38,89	0,15
16	10,9	50	127,08	2,50%	56,04	56,75	1,27
17	10,9	400	126,53	2,50%	49,91	49,66	0,50
18	**11,2**	**225**	**121,67**	**2,50%**	**45,74**	**44,85**	1,95
19	10,8	50	121,75	0%	50,26	50,38	0,24
20	11,3	400	121,78	0%	44,81	45,19	0,85
21	10,3	50	121,61	5%	48,94	48,96	0,04
22	11,2	400	120,78	5%	44,12	44,01	0,25
23	6,4	225	117,02	2,50%	34,42	34,81	1,13
24	15	225	116,82	2,50%	46,44	46,65	0,45
25	6,5	225	126,62	2,50%	44,32	44,5	0,41
26	15,1	225	126,82	2,50%	57,08	57,12	0,07
27	**10,8**	**225**	**121,6**	**2,50%**	**45,6**	**44,76**	1,84

THANK YOU

Questions or Comments
For Art and Sergio ???