Supercritical Washing of Polymers within a Twin Screw Extruder

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Overview

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  - Stripping-Enhanced Devolatilization
  - Liquid Extraction
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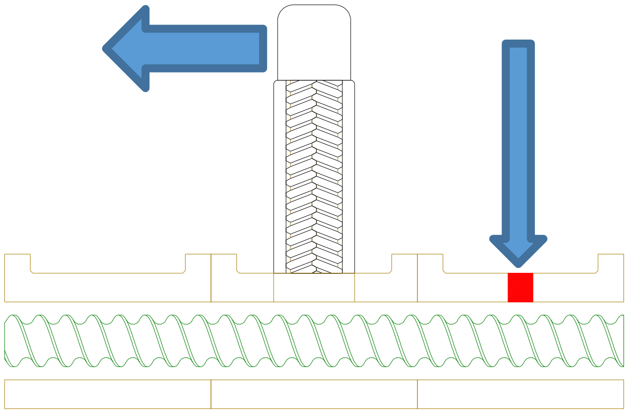
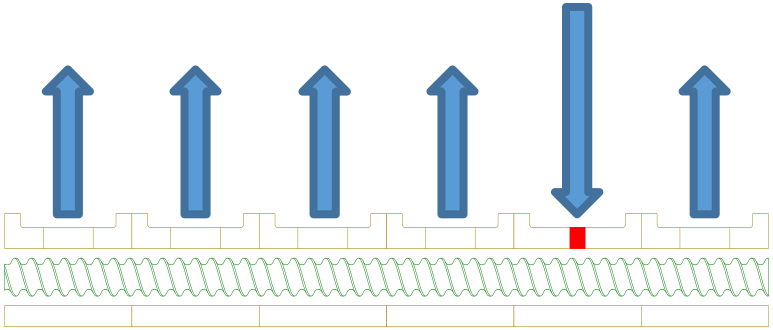
- Experimental
  - Materials and Equipment
  - Experimental Design
  - Results
- Discussion/Conclusions
- Questions



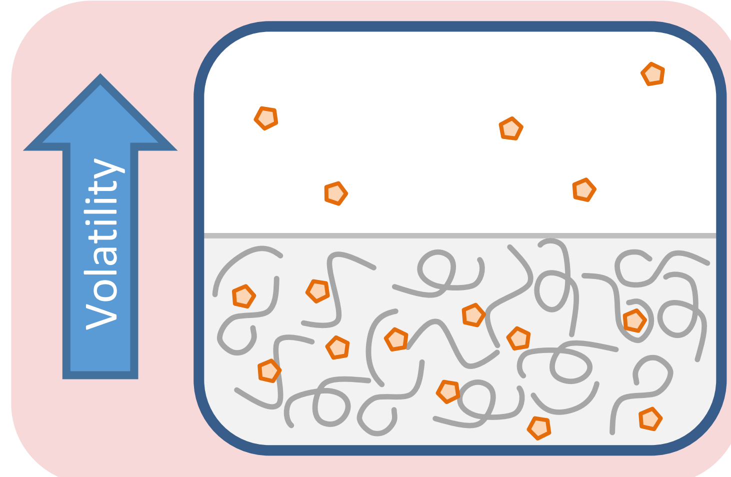
Purpose

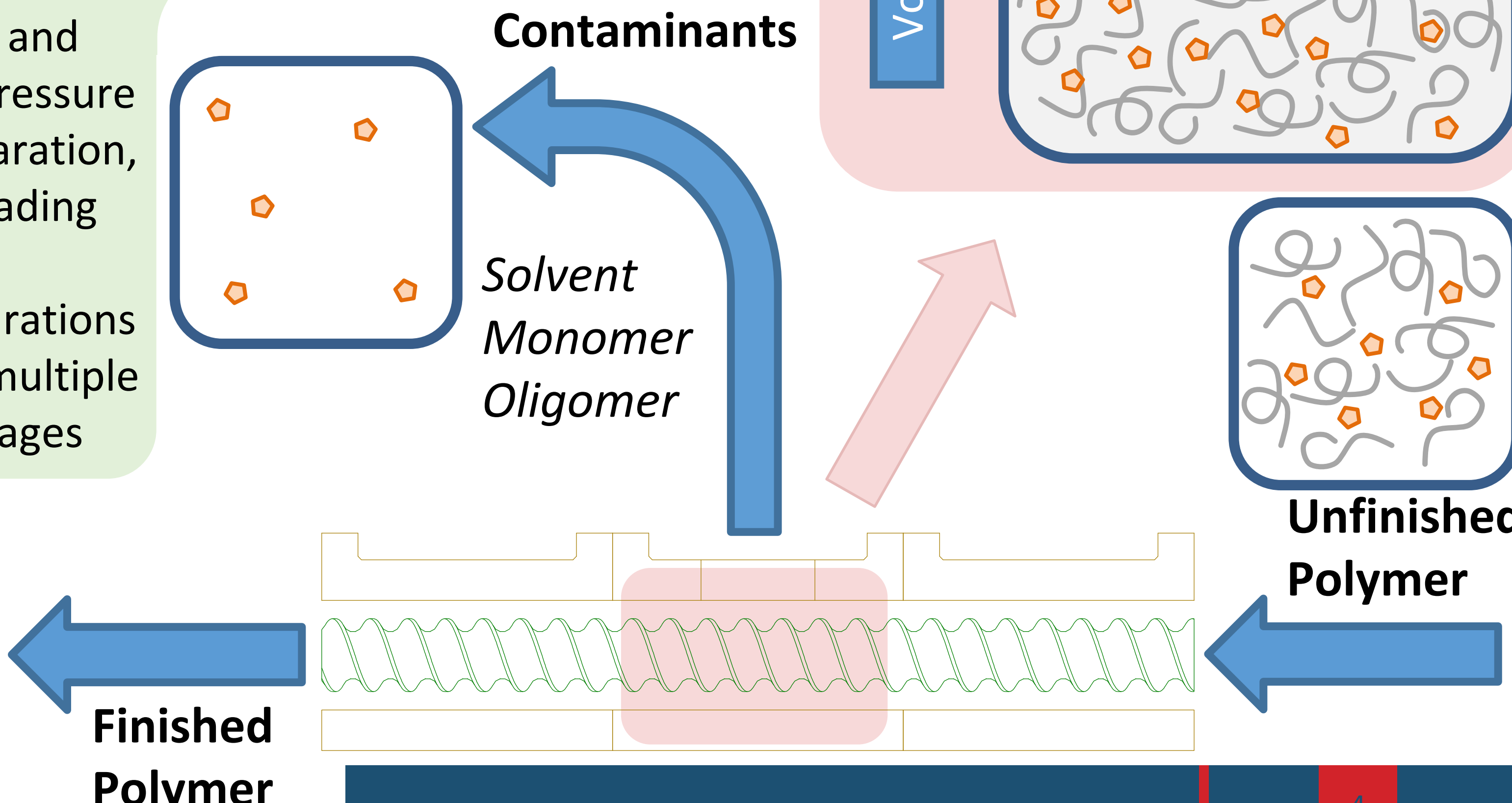
- Twin screw extruders (TSE) are a common separation unit operation
- The most typical TSE separation process is vacuum devolatilization
- Vacuum devolatilization relies on contaminant volatility to drive the separation
- Some contaminants have low volatility, requiring stronger vacuum, higher temperatures, and/or more stages of separation
- *The purpose of this presentation is to describe a process for purifying polymers using supercritical fluid as an* ***extraction solvent****—as opposed to a stripping agent*

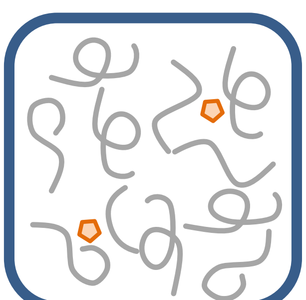


Devolatilization

- Vacuum is pulled on vents, vaporizing contaminants
- The driving force is volatility: $w_0 \rightarrow w_e$
- Rate determined by boiling and diffusion
- Increasing temperature and decreasing pressure improve separation, but risk degrading polymer
- Difficult separations can require multiple sequential stages







Driving Force: Volatility

Equilibrium Concentration:

$$w_e = \frac{P}{P_{sat}}\left(\frac{\rho_s}{\rho_p}\right)e^{-(1+\chi)}$$

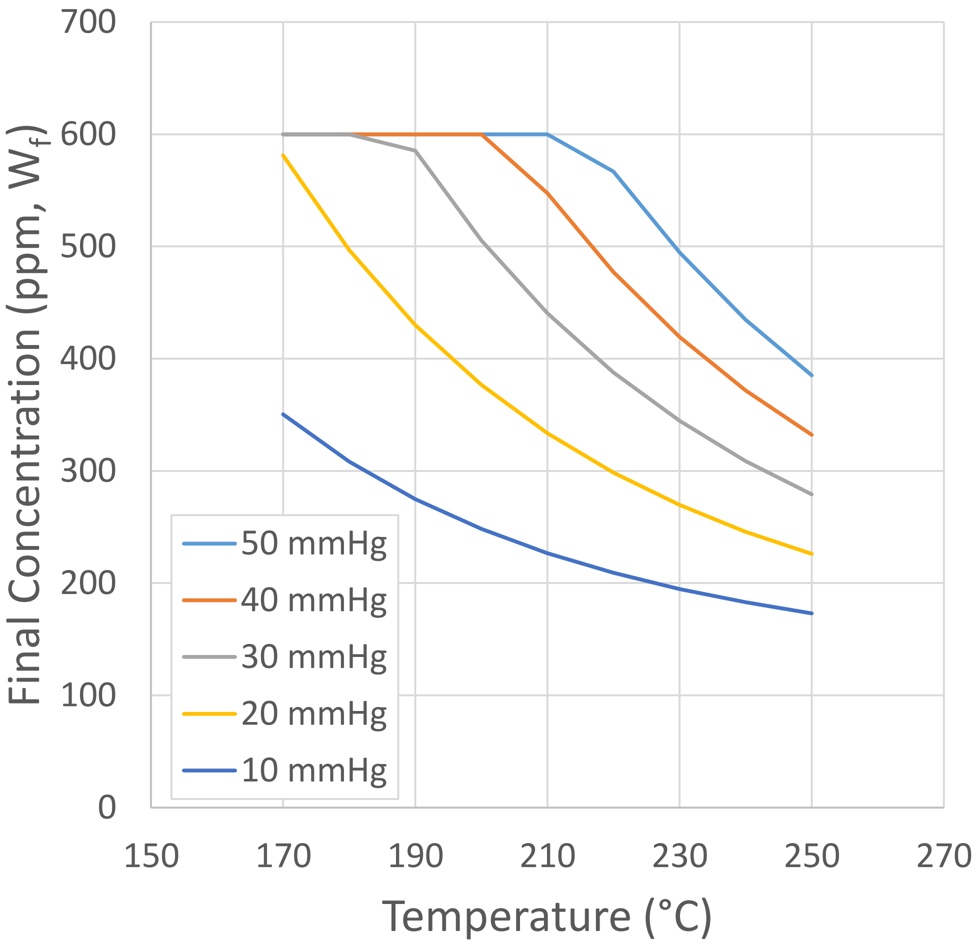
Final Concentration:

$$w_f = w_0 - E(w_0 - w_e)$$

Feed Concentration, $w_0 = 600$ ppm

Vent Pressures, $P = 10, 20, 30, 40, 50$ torr

Efficiency, $E = 80\%$



Effect of a Stripping Agent

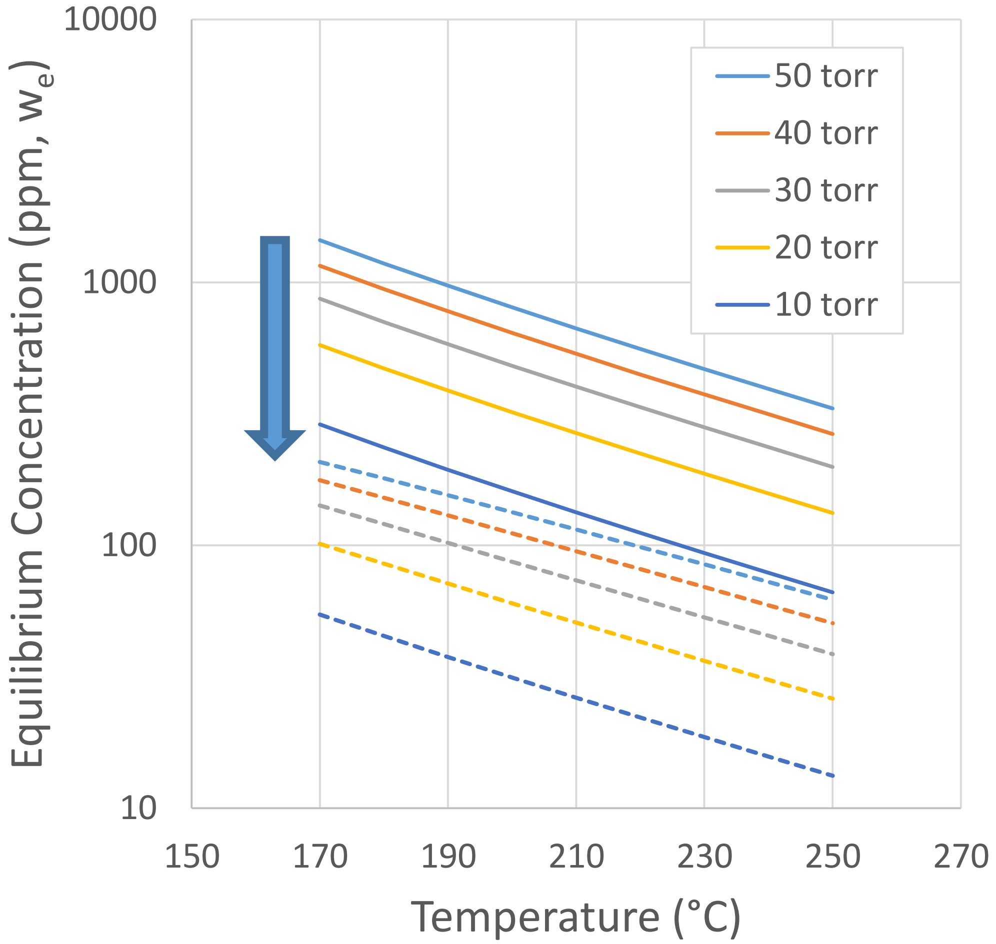
Equilibrium Concentration:

$$\begin{cases} n_G = \dfrac{w_0 - w_e}{w_0 - w_e + w_a \dfrac{MW_s}{MW_a}} \\ n_G = w_e \dfrac{P_{sat}}{P}\left(\dfrac{\rho_p}{\rho_s}\right) e^{(1+\chi)} \end{cases}$$

Introduce stripping agent, $w_a = 500$ ppm

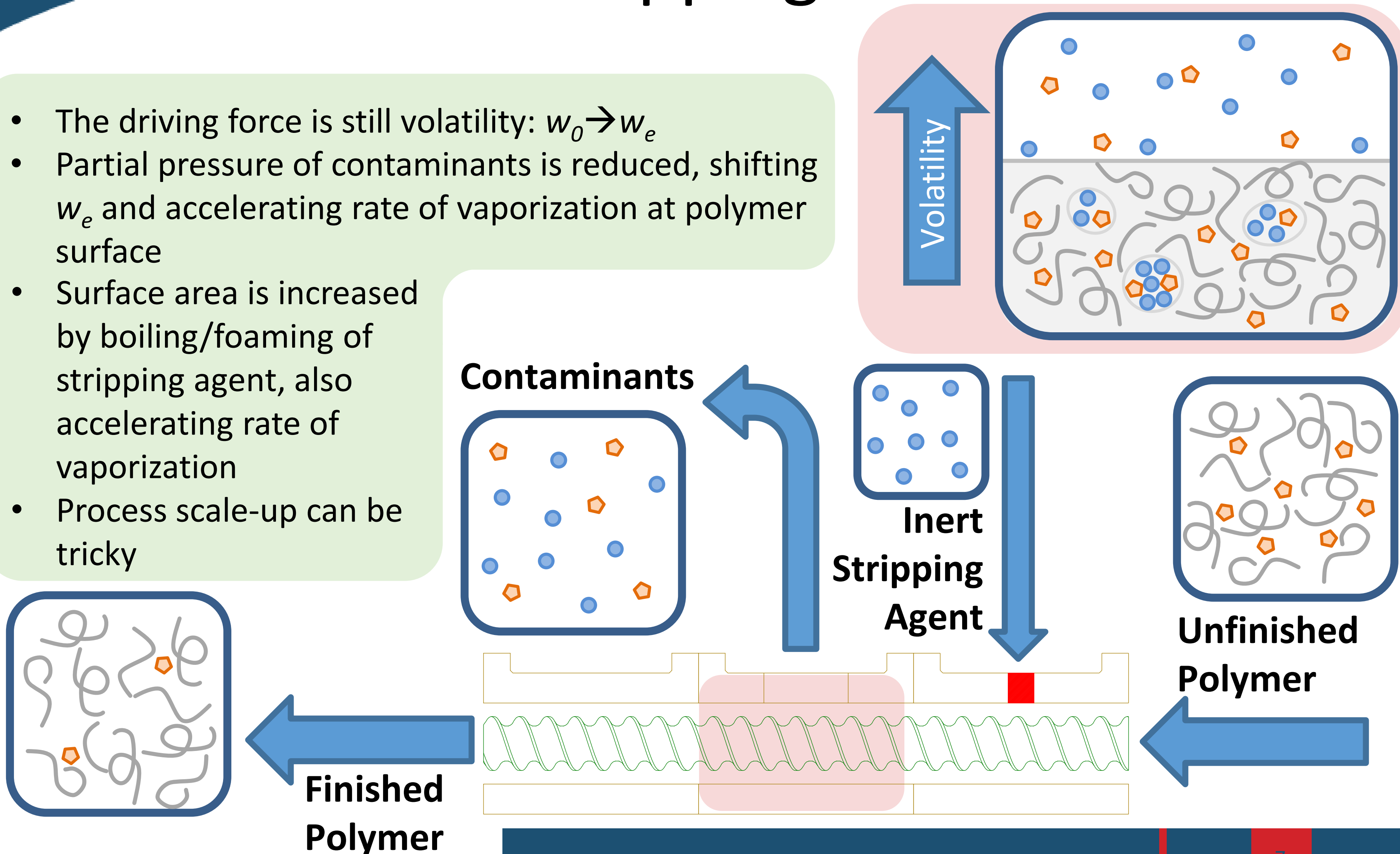
Solve for n_G, mole fraction in vapor phase

Equilibrium concentration, w_e, is significantly reduced



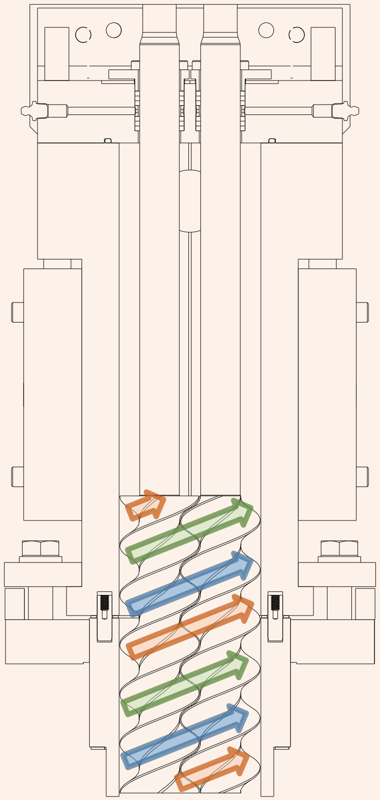
Stripping-Enhanced Devol

- The driving force is still volatility: $w_0 \rightarrow w_e$
- Partial pressure of contaminants is reduced, shifting w_e and accelerating rate of vaporization at polymer surface
- Surface area is increased by boiling/foaming of stripping agent, also accelerating rate of vaporization
- Process scale-up can be tricky



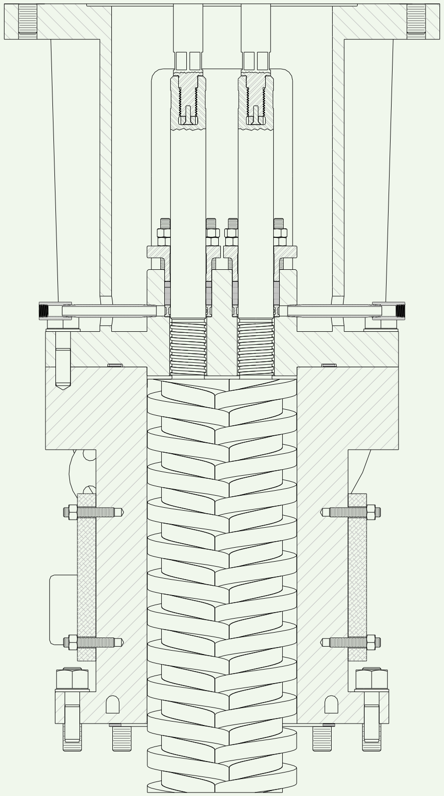
Mechanical Filter

Co-Rotating Vent Stuffer



- Typical vent stuffer design is co-rotating
- Similar to side feeder design
- Good for low vapor rate to prevent vent fouling
- Unable to separate solids and liquids

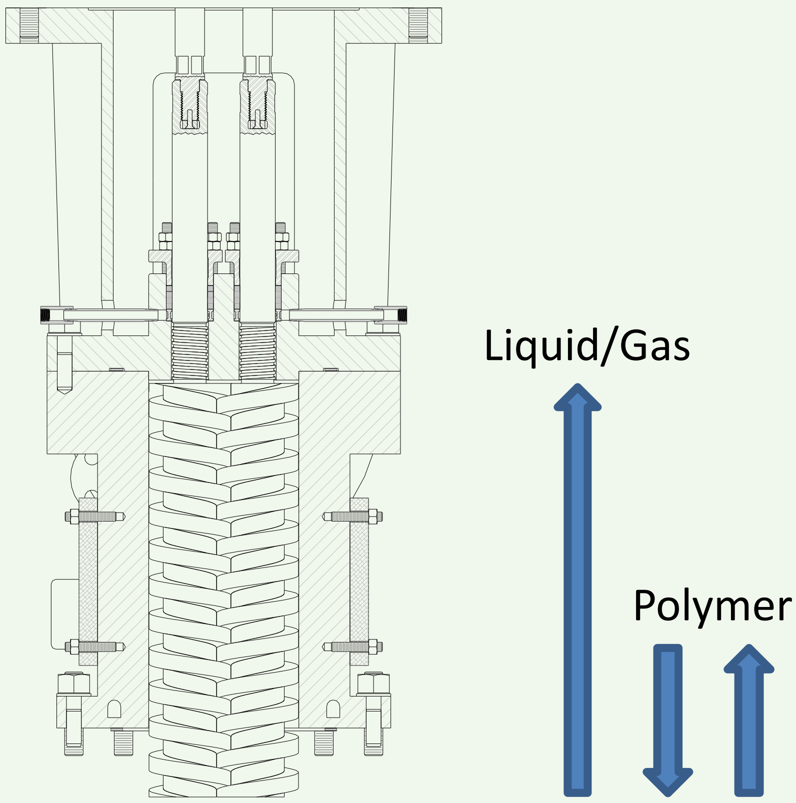
Counter-Rotating Mechanical Filter



- Separates low-viscosity fluids from high-viscosity fluids and solids
- Designed for flow rates between 5 and 500% of process polymer throughput
- Interlocking channels prevent escape of particles larger than ≈2mm

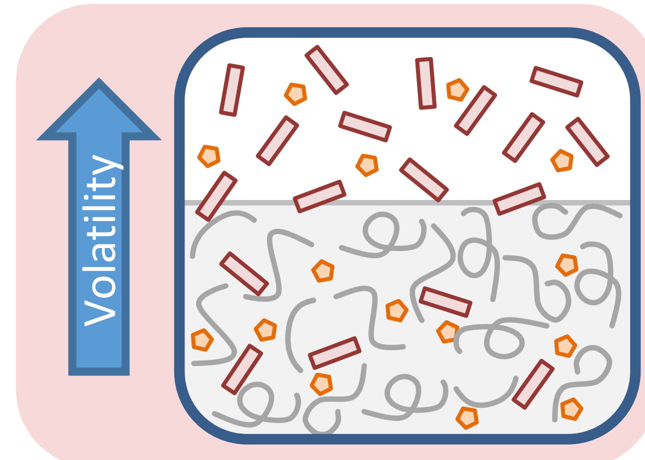
Mechanical Filter

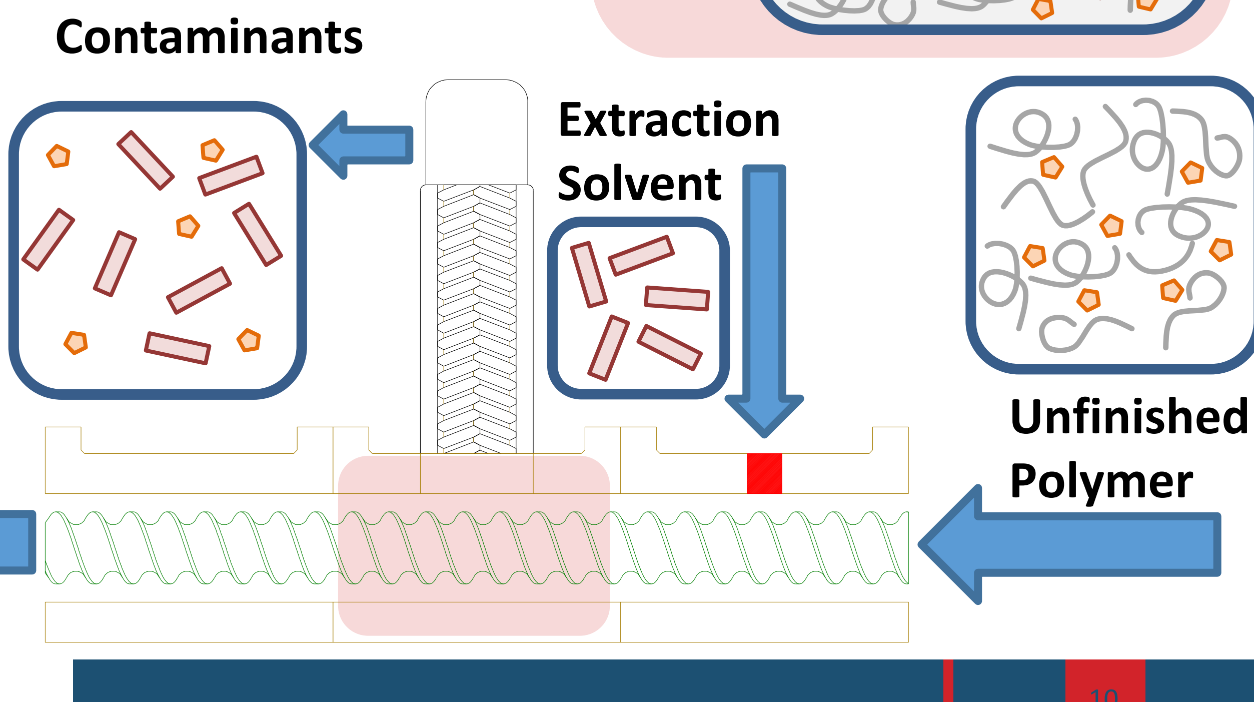
Counter-Rotating Mechanical Filter

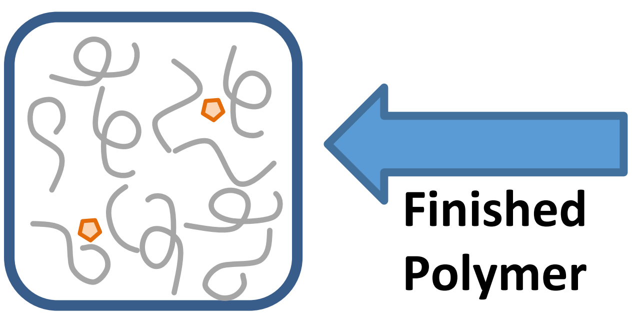


Liquid Extraction

- The driving force is solubility of contaminants
- Solvents that have some solubility in the polymer will swell the polymer phase, accelerating the rate of diffusion
- Non-volatile contaminants can be extracted
- Significant melt temp reduction
- Solubility of solvent will lead to carry-over, requiring additional separation stages

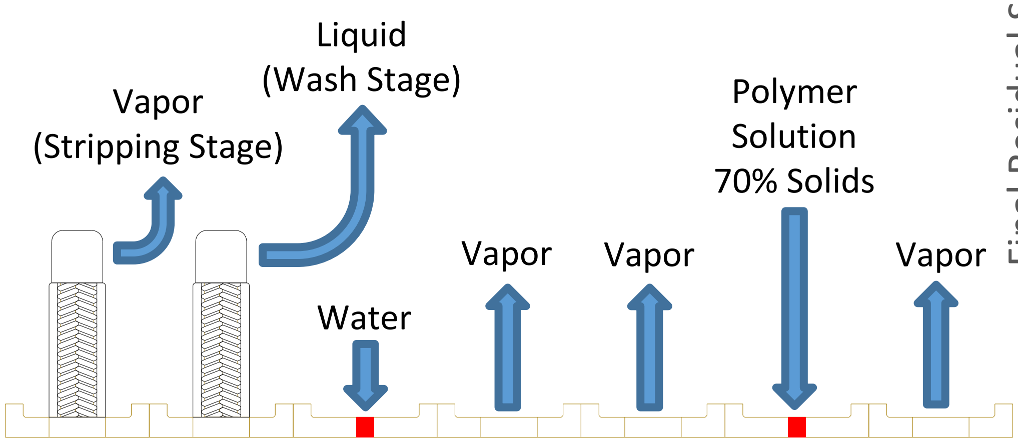


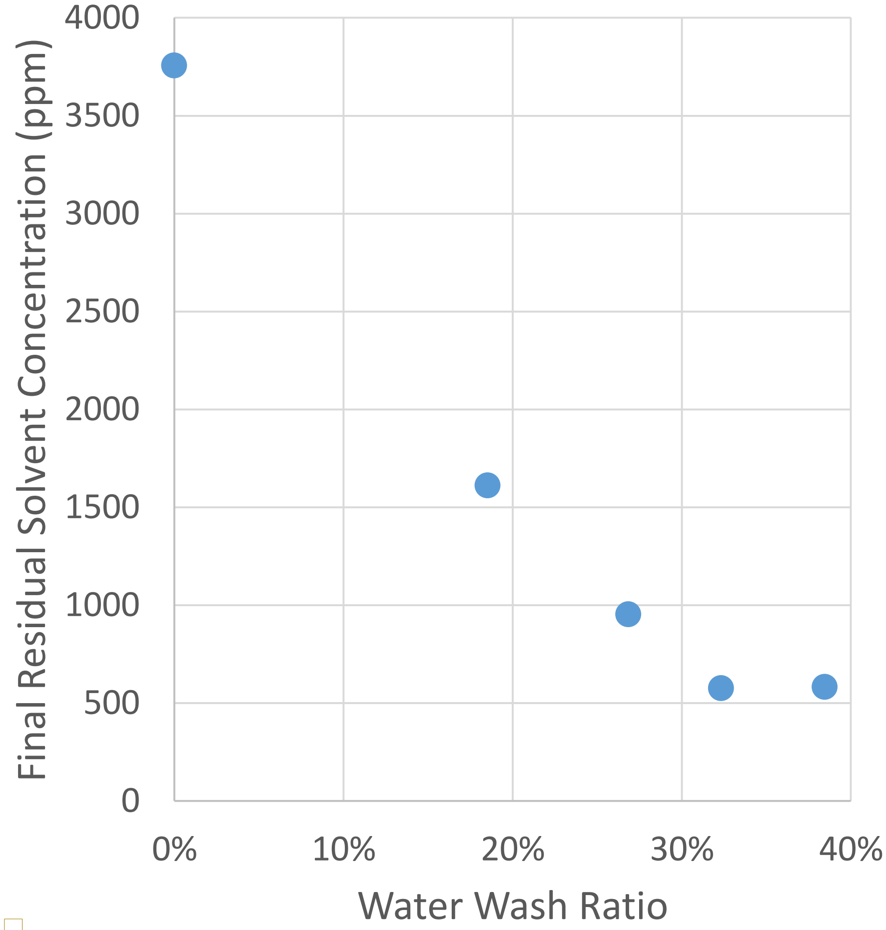




Solution Devol with Water Wash

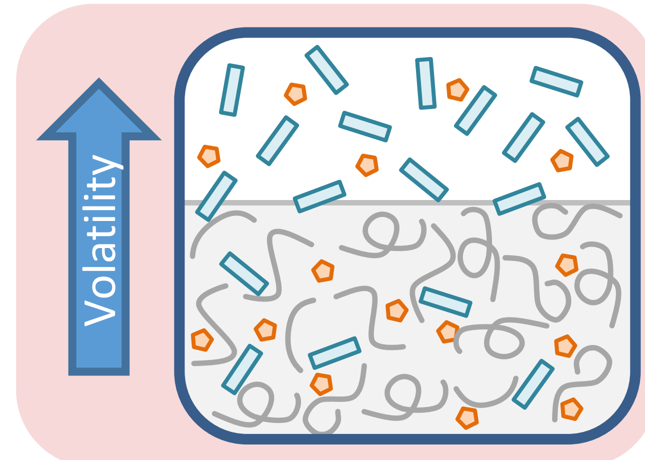
- Styrenic Block Copolymer, MFR≈60 dg/min
- 2” Counter-rotating non-intermeshing (CRNI) twin screw extruder
- 70% solids solution feed
- Three vent stages followed by water injection and two mechanical filters
- Significant residual solvent reduction
- Melt temperature reduced by 50°C

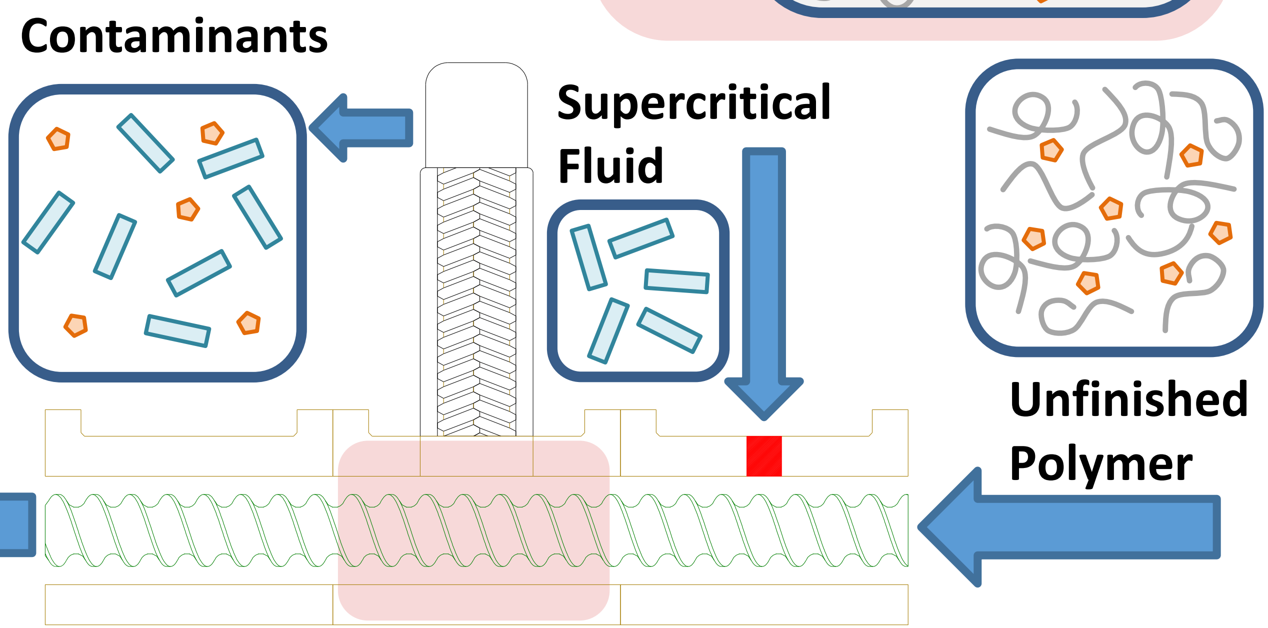


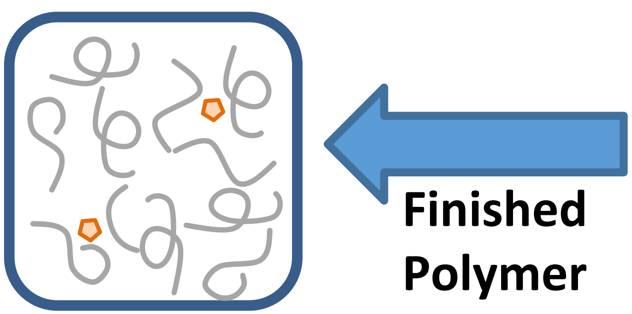


SCF Extraction

- The driving force is solubility of contaminants
- Solvents that have some solubility in the polymer will swell the polymer phase, accelerating the rate of diffusion
- Non-volatile contaminants can be extracted
- Solubility of solvent will lead to carry-over, which acts as excellent foaming stripping agent in subsequent stage







Comparison

	Pro	**Con**
Vacuum Devolatilization	• Low complexity • Effective for highly volatile impurities	• Difficult to control temperature • Driving force depends on volatility Rate is limited by diffusion below bubble point of impurity (no foaming)
Stripping	• Foaming is induced, which improves separation	• Vent fouling can be an issue for high gas/vapor flow rates • Driving force depends on volatility • Rate is limited by diffusion below bubble point of impurity (no foaming) • Can be difficult to scale • Adding melt seals increases shear and temperature
Liquid Extraction	• Scales well • Melt temp can be reduced significantly • Solubility in polymer will accelerate diffusion • Low-volatility impurities can be effectively removed	• Carry-over of extraction solvent requires additional downstream separation stages
SCF Extraction	• Scales well • Melt temp can be reduced significantly • Solubility in polymer will accelerate diffusion • Low-volatility contaminants can be effectively removed • Carry-over of extraction solvent improves downstream venting by encouraging foaming	• Increased complexity • SCF may need to be recycled • High pressure must be contained within extruder

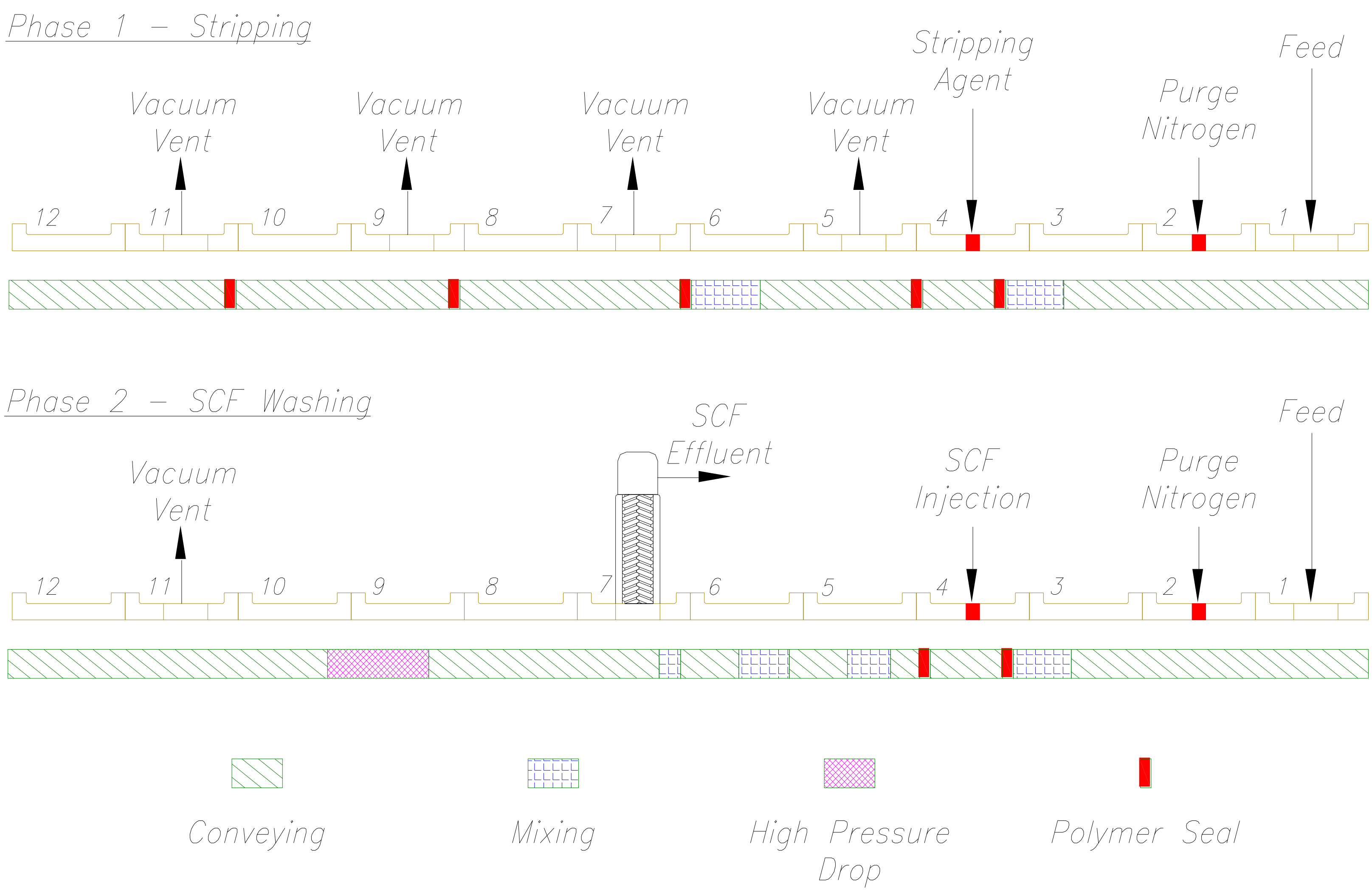
Experimental Design

Goal: Reduce outgassing organics in commercial grade of polypropylene

- Phase 1: Stripping
  - Four Stripping Media:
    - Nitrogen
    - Carbon Dioxide
    - Methanol
    - Water
  - Two Stripping Ratios:
    - 1% w/w
    - 3% w/w

- Phase 2: SCF Washing
  - Two Washing Fluids:
    - Nitrogen
    - Carbon Dioxide
  - Two Washing Ratios:
    - Low (32 wt%)
    - High (41 wt% (N_2) or 48 wt% (CO_2))

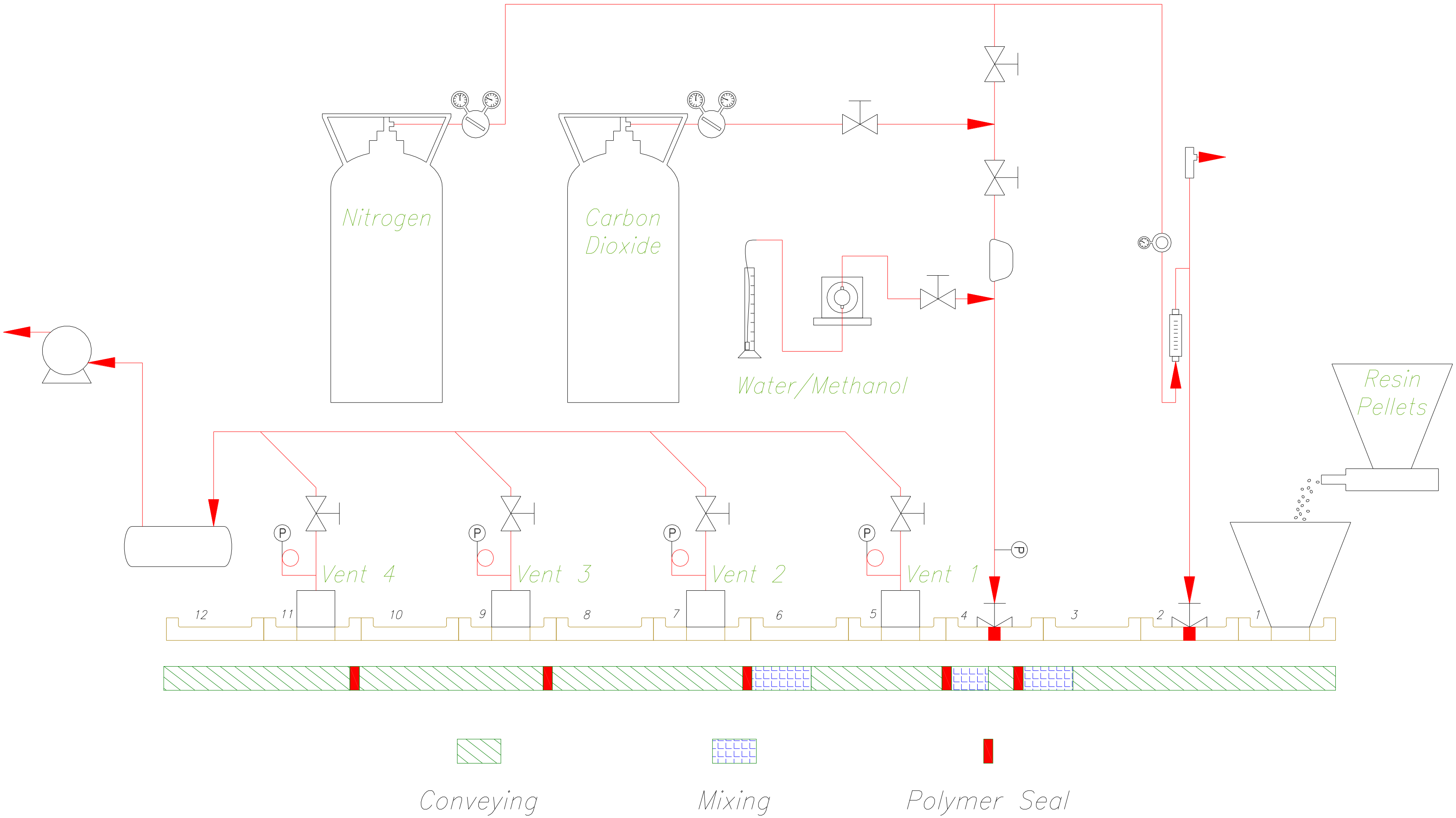
Experimental Design



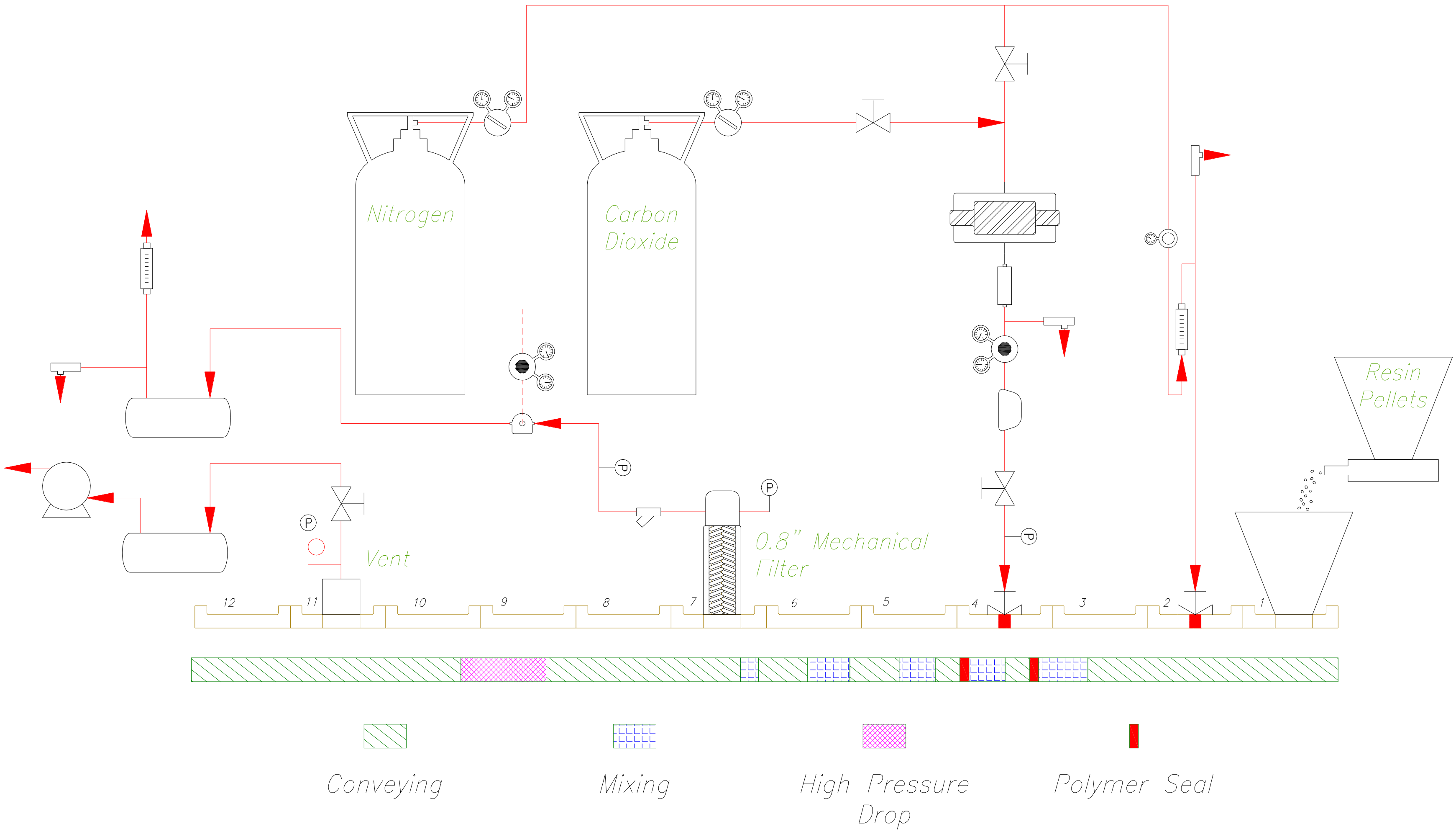
Equipment – Twin Screw Extruder

- NFM TEM-26SS Co-Rotating Twin Screw Extruder
  - 48 L/D – Twelve 4 L/D segments
  - Barrels lined by HIP with NFM-24
  - Cored for cooling with water
  - Heated by cast aluminum electric heaters

Phase 1: Stripping

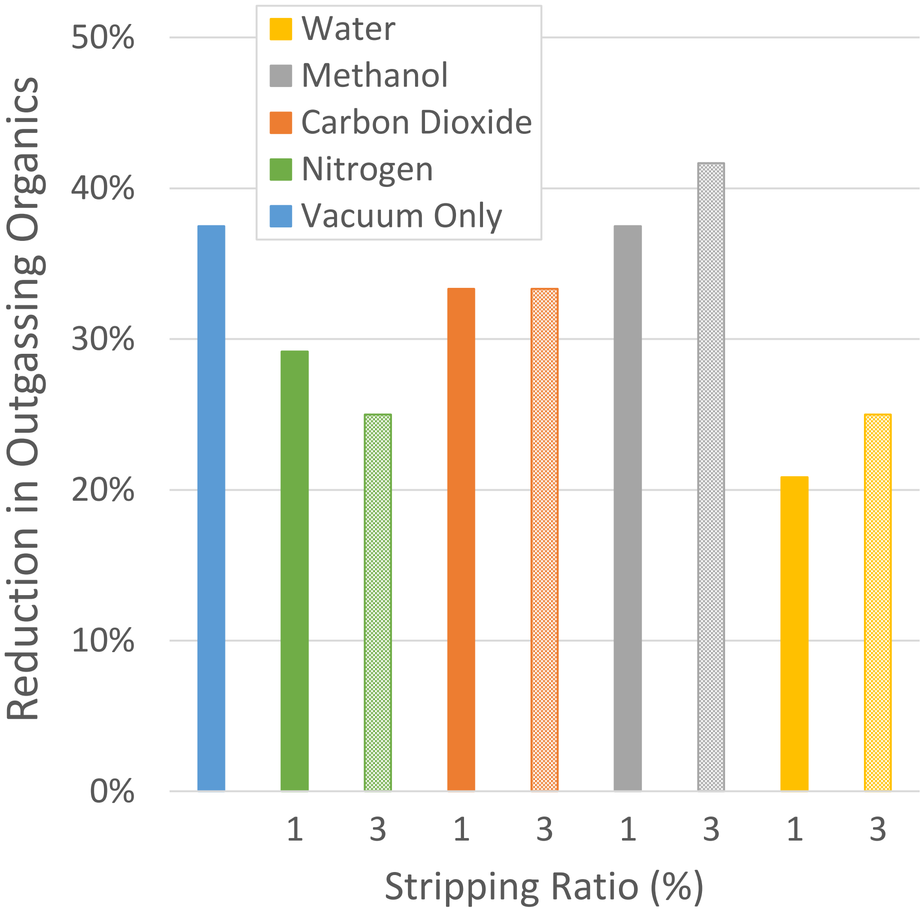


Phase 2: SCF Washing



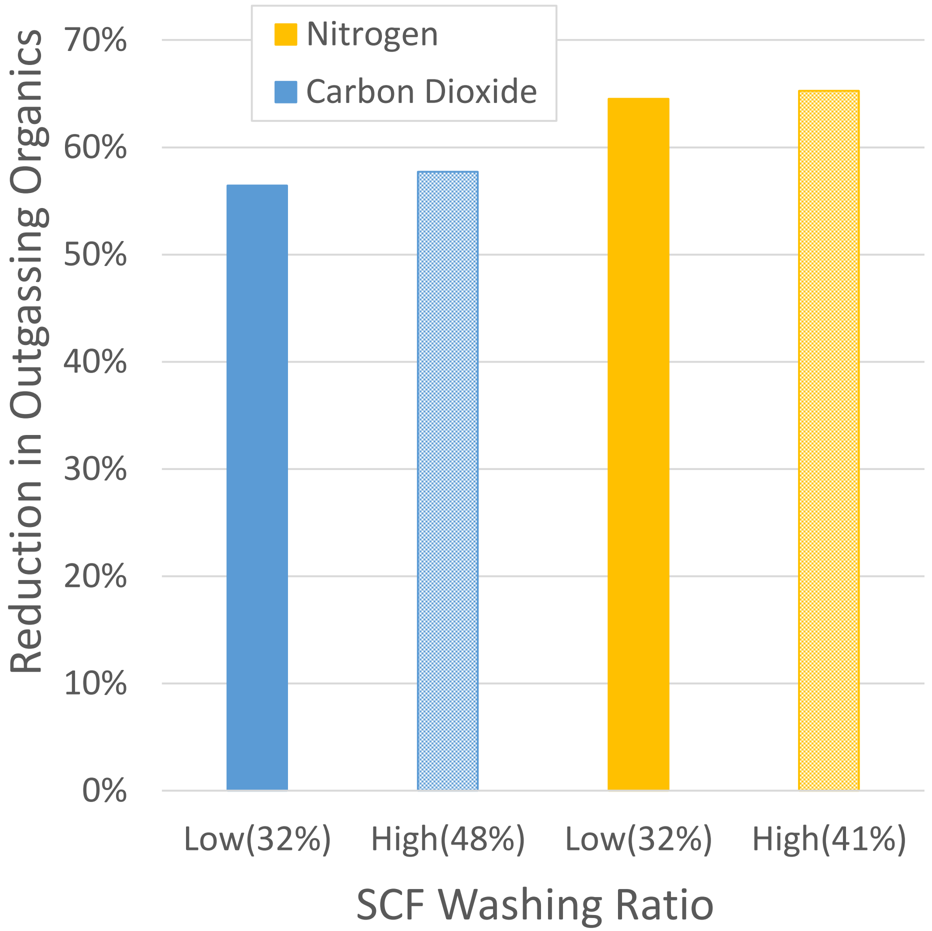
Phase 1: Stripping – Results

- Vacuum venting alone achieved a 38% reduction in outgassing organics
- Stripping with water, methanol, nitrogen, and carbon dioxide did not demonstrate an improvement compared to vacuum alone
  - The only exception was methanol at 3%
- Increasing the stripping ratio from 1% to 3% showed no effect for carbon dioxide, and adversely affected outgassing reduction for nitrogen
- Increasing the stripping ratio from 1% to 3% improved outgassing reduction for water and methanol.



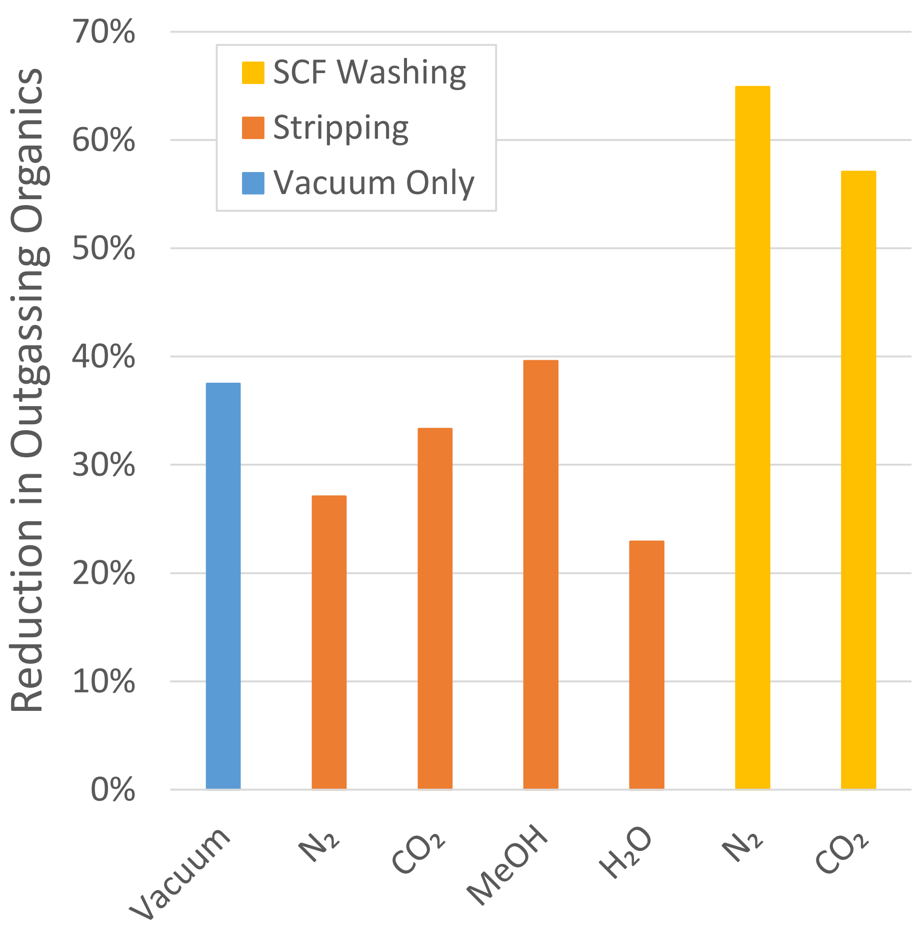
Phase 2: SCF Washing – Results

- Supercritical carbon dioxide and nitrogen each significantly reduced the level of outgassing organics
- Nitrogen was more effective than carbon dioxide (65% vs 57% reduction)
- Increasing the SCF ratio from 32 wt% to 41/48 wt% did not significantly improve washing performance



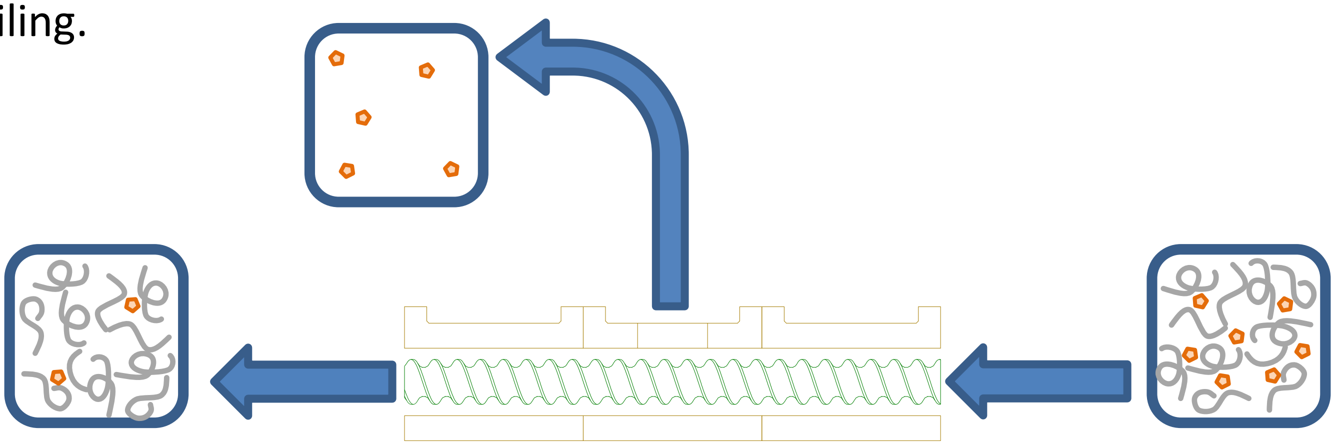
Phases 1 & 2: Combined Results

- Vacuum devolatilization alone was very effective for reducing outgassing organics for the grade of commercial polypropylene tested
- Stripping did not demonstrate any significant gains over vacuum alone, except for methanol at 3%
- Washing with supercritical carbon dioxide and nitrogen was very effective compared to vacuum alone and stripping with the four agents evaluated



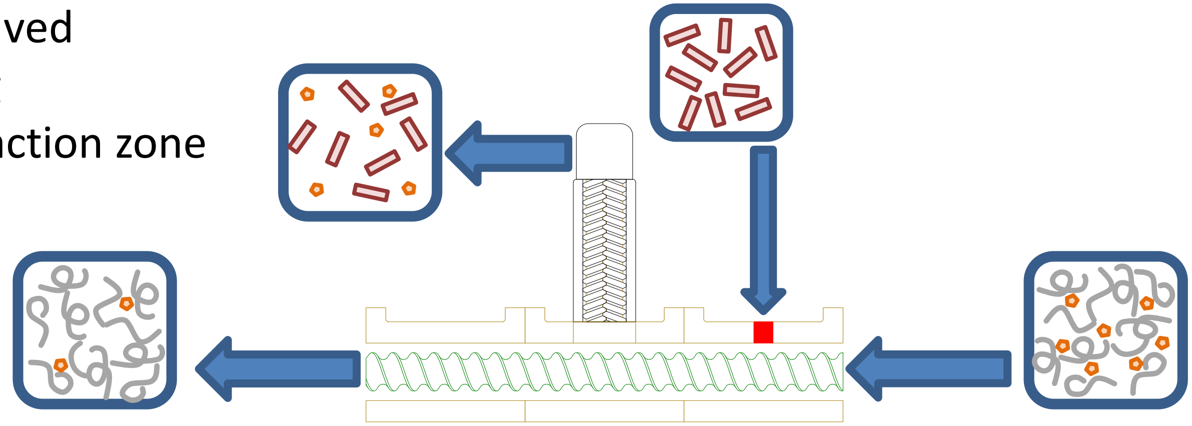
Discussion and Conclusions

- Polypropylene had relatively low organic residuals, known to comprise a range of short chain oligomers with low vapor pressures.
  - Vacuum alone was able to remove 38% of the most volatile outgassing organics.
- Compared to vacuum alone, stripping was ineffective, if not counterproductive.
- Methanol likely dissolved more successfully into the polymer melt than water, nitrogen, or carbon dioxide under the processing conditions, which would have enhanced foaming.
- Water stripping performed the worst of all conditions tested. This could be attributed to the poor compatibility of PP and water, and the high latent heat of water, which will result in melt cooling on boiling.



Discussion and Conclusions

- Supercritical fluid washing performed very well compared to vacuum alone and traditional stripping.
- Vacuum devolatilization was able to remove 38% of outgassing organics in four vent stages.
- These components likely had the highest vapor pressures, leaving behind higher molecular weight oligomers.
- With only one vacuum stage, SCF extraction was able to improve the reduction of outgassing organics by an additional 30%.
- Some of this improvement can be attributed to the rapid expansion of dissolved nitrogen/carbon dioxide during decompression out of the extraction zone



Questions?