Assessing Technical Feasibility of Supercritical Extraction Processes Utilizing Laboratory Equipment

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Introduction

- Efficient Commercial-Scale SFE Plant Process Development Requires Utilizing Two High Pressure Laboratory Instruments
  - Variable Volume Equilibrium Cell
  - Benchtop SFE Extraction Unit
- Variable Volume Equilibrium Cell
  - Can Be Used to Determine Solubility (especially useful for multi-component mixtures)
  - Can Be Used to Determine Precipitation Operating Conditions for Design of Separators

Introduction (continued)

- Benchtop SFE Extraction Unit
  - Useful for Determination of Extraction Rates, Solvent/Feed Ratios, and Determining Extractor Operating Conditions Such as Pressure and Temperature
  - Also Useful for Optimizing Pretreatment Processes (e.g. Grinding, Flaking, Soaking, Drying, etc.)
  - Useful for Changing Process Variables for Product Development and Producing Product Samples

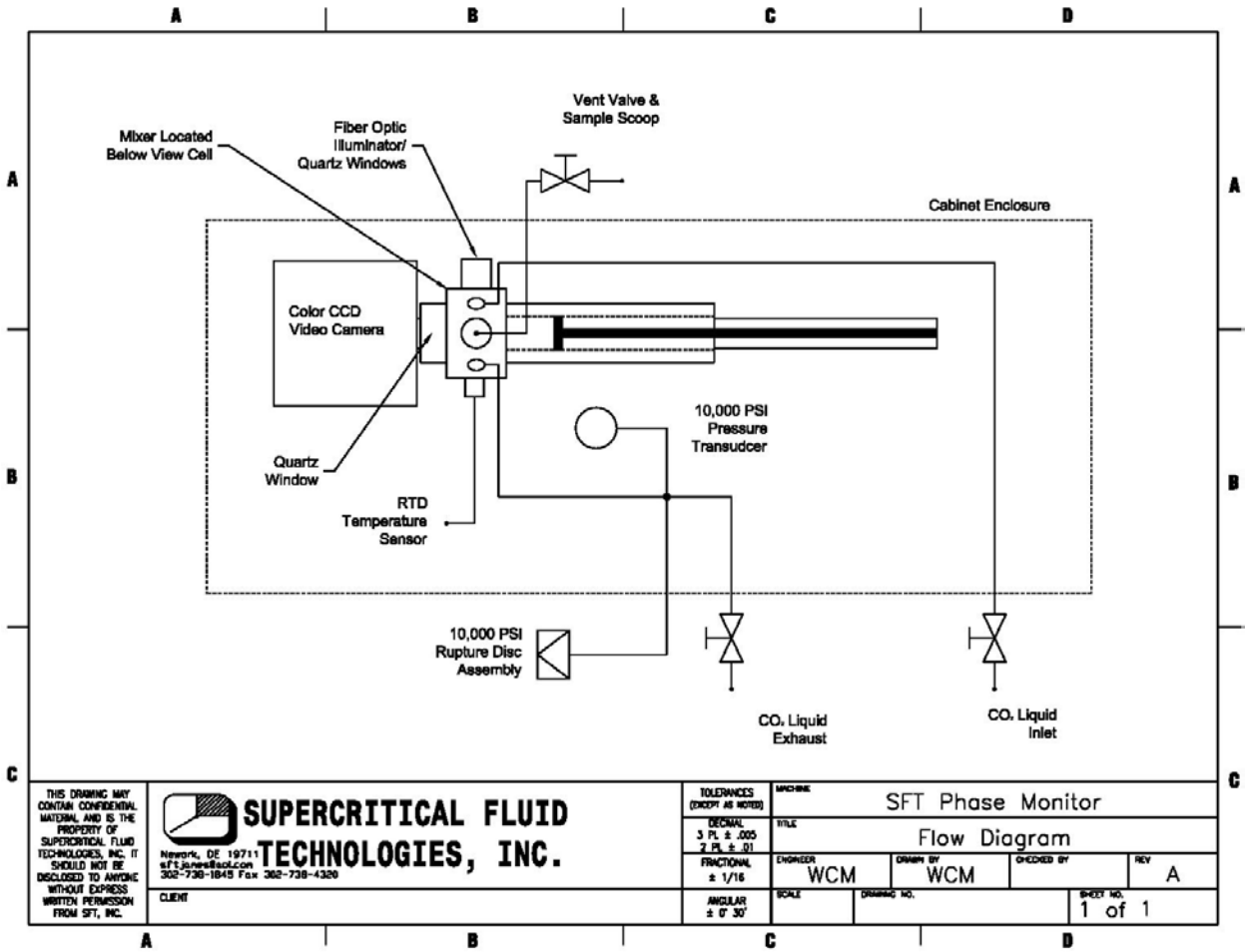
First Step: Determining Solubility

- Solubility Measurements of Solutes in Supercritical Fluids are Extremely Useful Data for Screening Potential Applications of SFE
- Phase Equilibria Data Important in Determining:
  - Optimal Operating Conditions for Fractional Extraction or Separation (selectivity)
  - Solvent/Feed Ratio
  - Optimal Supercritical Fluid and Concentration of Co-Solvent

Variable Volume Equilibrium Cell

- SFT Phase Monitor II:
  - Provides Direct, Visual Observation of Dissolution, Precipitation and Crystallization of Compounds Over a Wide Range of Pressures and Temperatures (Subcritical or Supercritical Conditions)
  - Researcher can Quickly Screen Pure Components and Mixtures to Determine Solubility Over a Wide Range of Pressures and Temperatures
  - Experiments May be Performed in Liquid or Supercritical Carbon Dioxide or in Other Compressed Gases.
  - The effect of Co-Solvents on the Solubility of Compounds of Interest in Supercritical Carbon Dioxide can be Investigated
  - Experiments can be Performed from a Few Hundred psi to 10,000 psi and from Ambient Temperature to 140º Centigrade
  - Conditions for Fractional Extraction and Separation of Mixtures of Compounds can be Investigated

Variable Volume Equilibrium Cell



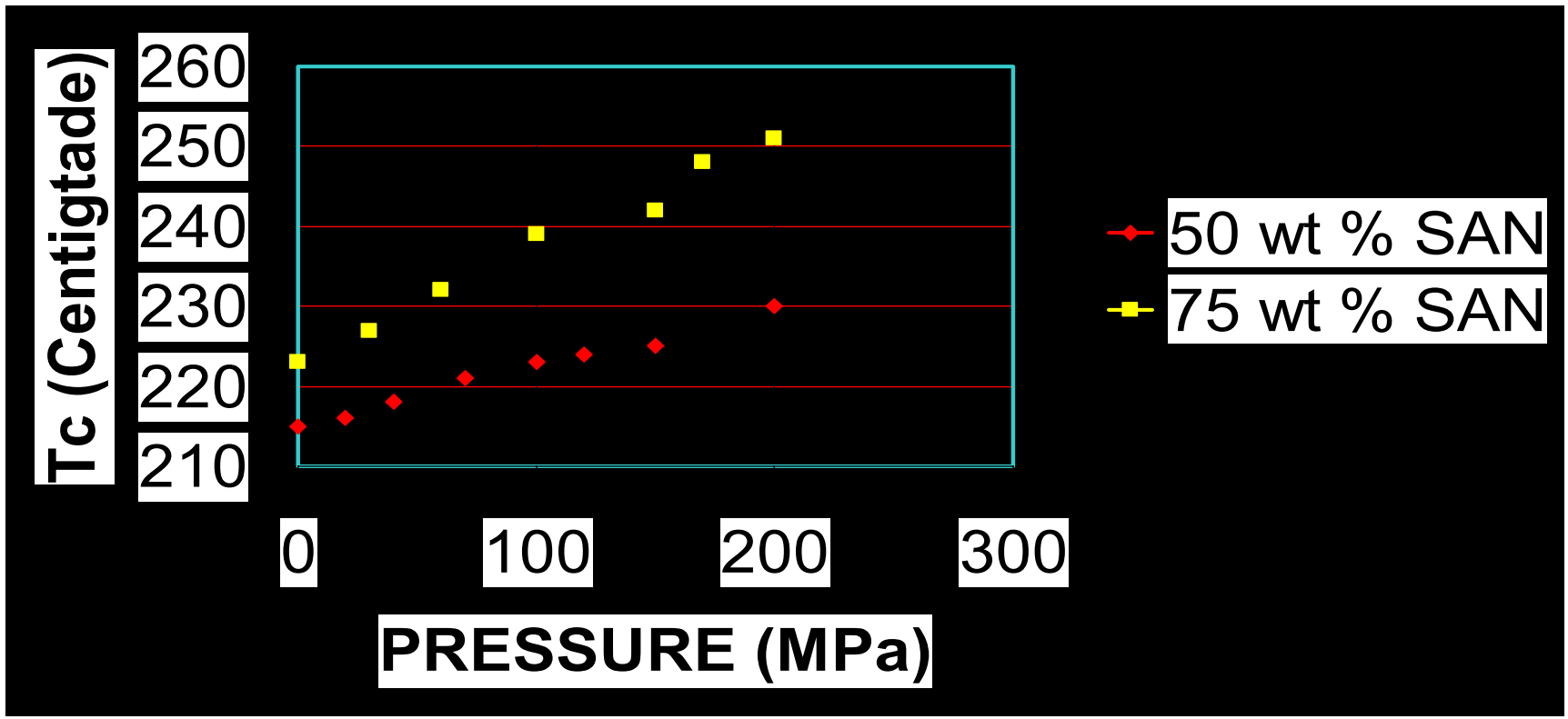
Variable-Volume Equilibrium View Cell Apparatus

- Main Components Include Variable-Volume Equilibrium View Cell, Hand or Motorized Pressure Generator, Light Source and Color CCD Video Camera
- Solid and Liquid Solutes Completely Solubilized Until Clear, Single Fluid Phase Observed; Mixture Decompressed Until Solid Precipitates and Two Phases Observed
- Apparatus Capable of Measuring Vapor Phase of Composition Only (solubility of solute in supercritical fluid)
- Not Useful for Solutes in Which Large Amount of CO_2 Dissolve in Liquid Phase (e.g. vegetable oils)

Variable-Volume Equilibrium View cell Apparatus

Typical Data From A Variable View Cell

- *Effect of Pressure on the Cloud Point Temperature (T_c) for Mixtures of SAN* and PMMA** (*poly(styrene-co-acronitrile)(**poly(methyl methacrylate)*



Li and Radosz, *Polymer Preprints*, 1992,33,422

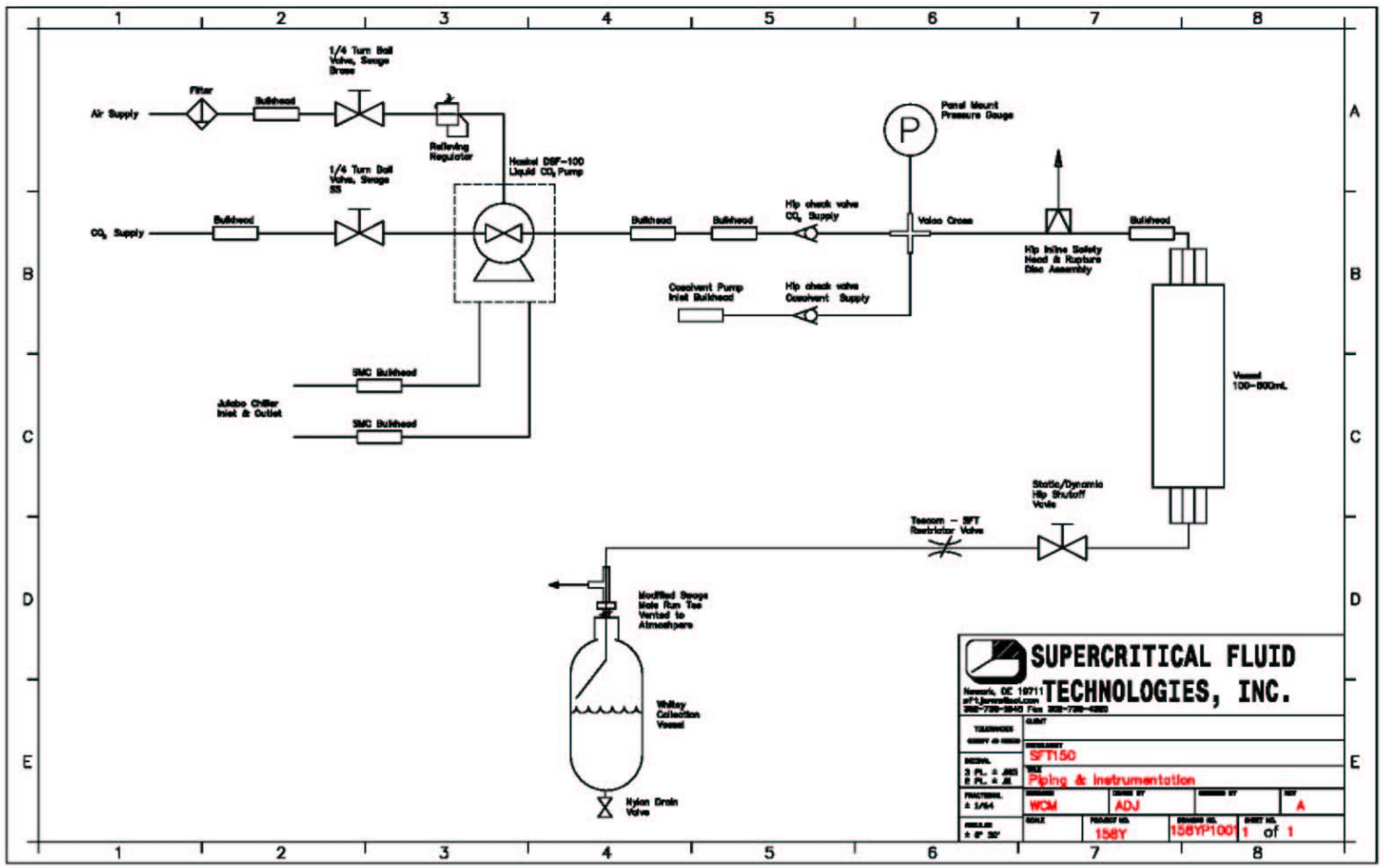
Benchtop SFE Unit

- Primary goal of Analytical/Laboratory SFE Unit Testing is to Assess Technical Feasibility of a Potential Supercritical Fluid Extraction Application.
- The Analytical/Laboratory Unit Typically has a 10 ml to 1 liter Extraction Capacity.
- Product Samples and Data From the Feasibility Testing Are Used to Assess Product Quality, and to Research Process Operating Parameters

Benchtop SFE Extractor

- Typical SFE Extractor Comprises - High Pressure Carbon Dioxide Pump, Extraction Cell, Heated Micrometering Valve, Atmospheric Collection Vessel and Flow Meter
- Solid Feedstock Placed in High Pressure Extraction Vessel and Carbon Dioxide Flows Through Extraction Vessel to Micrometering Valve
- Micrometering Valve Depressurizes Supercritical Fluid to Gas State and Solutes Precipitate in Collection Vessel

Schematic of an SFE Unit



Benchtop SFE Apparatus

Process Parameters Investigated on Benchtop SFE Unit

- Preparation of Feedstock
  - Grating
  - Grinding (cryogrinding)
  - Flaking
  - Pelletizing
  - Drying
  - Wetting
  - Rapid Depressurizing

Process Parameters Investigated on Benchtop SFE Unit continued

- Extractor Conditions
  - Pressure
  - Temperature
  - Solvent Selection
  - Cosolvent Selection and Concentration
  - Flow Rate
  - Vessel Aspect Ratio
  - Solvent/Feed Ratio

Process Parameters Investigated on Benchtop SFE Unit conditions

- Separator Conditions
  - Pressure
  - Temperature
  - Adsorbent Separation
  - Membrane Separation
  - Filter Separation
  - Centrifugal Separation
  - Fractional Separation

Typical Parametric Investigation of Extraction Conditions on Lab SFE Unit

Saw Palmetto Extraction Data to Determine Extractor Operation Conditions

Temp (C)	Pressure (psig)	Solvent/Feed Ratio	Yield (1%)
80	Liquid	10	ND
	3150	30.55	14.46
	5120	18.33	15.13
	8000	18.33	15.07
	9540	18.33	15.27
60	Liquid	10	ND
	3040	27.5	15.6
	5040	18.33	15.13
	7500	18.33	14.86
	9640	18.33	13.33
40	Liquid	10	ND
	3160	27.5	15.86
	5200	18.33	15.27
	7600	18.33	15.6
	9540	18.33	15.13

240 x Scale-Up of Laboratory SFE Data

Comparison of Lab Scale and Pilot Plant Results

		Lab-Scale		Pilot Plant	
Pressure	Temp (C)	SF-Ratio	Yield (%)	SF-Ratio	Yield (%)
5100	60	18.33	15.13	20.0	14.8
8000	80	18.33	15.07	20.0	16.0
9500	80	18.33	15.27	10.0	16.0

Conclusion

- Benchtop Phase Equilibrium Monitor and SFE Unit Useful for Process Development to Determine Extraction/Separation Operating Conditions
- Variable-Volume Equilibrium View Cell Apparatus Accurate and Quick Method for Obtaining Solubility/participation Data (especially with multi-component mixtures)
- Benchtop SFE Unit is Remarkably Accurate for Determining Extraction Rate Data for Preliminary Economic Analysis of a Commercial-Scale Application.