Extraction of Natural Ingredients from Natural Feedstock's Using Supercritical Fluids

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Abstract

Supercritical fluid technology is especially attractive for extraction of natural ingredients when extraction and fractionation can be accomplished simultaneously in the high pressure process. This can be accomplished effectively when optimized process operating and separation conditions are selected. Supercritical fluid technology is useful for manufacturing products of standardized concentration of active ingredients, and products of much higher concentration (higher yields and purity)and quality (with less creation of artifacts), than possible by conventional chemical engineering unit operations such as liquid/liquid extraction, steam distillation, mechanical micronization.

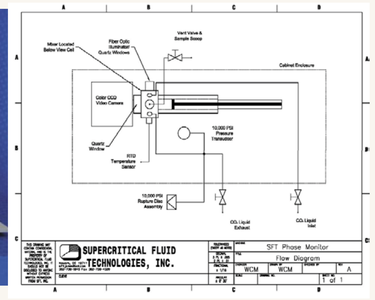
Product samples and data from the SCF feasibility testing are used to assess product quality, and to research the following process variables: 1) Preparation of feedstock 2) Extractor conditions 3) Separator conditions. The extract product is analyzed to determine how changes in these parameters change extract yield, concentration, and quality. Phase equilibrium experiments are carried out to determine the preliminary processing conditions in which the compound of interest solubilizesand precipitates from the supercritical fluid. This information can then be utilized to give a "starting point"to the extraction and separator processing conditions and insight to a commercial scale supercritical fluid extraction system. This poster illustrates the selection of operating conditions to maximize both yield and selectivity utilizing several examples.

Solubility Experiments –Phase Monitor

Direct, visual observation of materials under supercritical conditions is an important first step in the development and refinement of supercritical fluid extraction, reaction, and chromatographic processes. A specially designed phase equilibrium view cell or "Phase Monitor"is used to observe the dissolution, melting, precipitation, swelling and crystallization of compounds at a wide range of pressures and temperatures. Observations of materials are performed in the supercritical region, under precisely controlled conditions. The Phase Monitor simplifies the determination of critical pointfor binary, tertiary or complex mixtures. Through a better understanding of phase behavior as a function of temperature, pressure, co-solvent, and sample concentration, a significant time and cost savings for supercritical process development is realized.

Variable-Volume Equilibrium View Cell Design

Main components include a Variable-Volume Equilibrium View Cell, Pressure Generator, Light Source and Color CCD Video Camera, sample mixing, and optional Video Monitor Display Panel Module, PC Video Capture Software, and Co-Solvent Addition Module. Experiments can be Performed from a FewHundred psi to 10,000 psi (689 Bar, 69 mPa) and from Ambient Temperature to 150odegrees Celsius.



Validation of Solubility Measurements

The accuracy of the SFT-Phase Monitor as an experimental method was validated by comparing the experimentally determined critical point for pure CO_2 with the literature values. The gradual phase transition of carbon dioxide from a single phase supercritical state through the critical point to a two phase subcriticalstate is pictured below. (The view cell shown here has a glass tube sample holder inserted in the cell).

Supercritical state

Critical Point

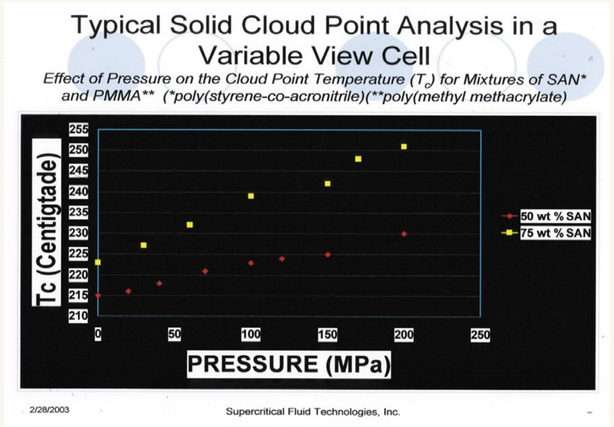
Subcritical state

Critical point of CO_2

	T_c/ K	P_c/bar
Literature	304.2	73.8
This work	304.1	73.6

Typical Example of Solubility Parameters Determination

Once the appropriate solubility parameters are obtained for a material at a given temperature, pressure, and co-solvent condition with the Phase Monitor, these data can then applied to give a "starting point"to the development of the true processing parameters in a supercritical fluid extraction unit. Pictured below are some typical cloud point data for the solubility of poly(styrene-co-acronitrile) and poly(methylmethacrylate). When the supercritical fluid and sample is clear, the sample is soluble, when there is a "cloud point"of the supercritical fluid and sample there is no (or minimal) solubility.



Supercritical Fluid Extraction Development Unit

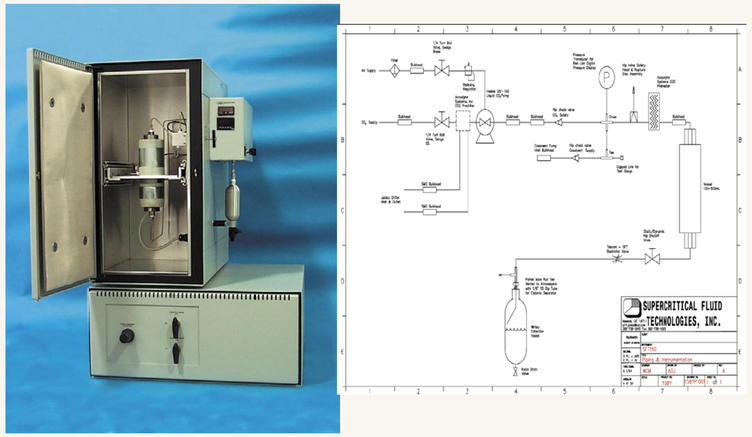
A typical SFE Extractor is comprised of a High Pressure Carbon Dioxide Pump, Fluid Preheater, Co-Solvent Addition Module, Extraction Sample Cell, Heated Micrometering Valve, Atmospheric Collection/Separator Vessel and Flow Meter. Solid Feedstock Placed in High Pressure Extraction Vessel and Carbon Dioxide Flows Through Extraction Vessel into the Micrometering Valve. The Micrometering Valve depressurizes the supercritical fluid (to the gas state) and the analyte of interest precipitate in the collection vessel

Key parameters for the processing of the raw material to achievethe desired quality and yield are detailed in the SFE unit.

Preparation of Feedstock: Grating, Grinding (cryogrinding), Flaking, Pelletizing, Drying, and Wetting

Extractor Conditions: Pressure, Temperature, Preheater settings, Solvent Selection, Co-solvent Selection (Concentration), Flow Rate, Vessel Aspect Ratio, and Solvent/Feed Ratio

Separator Conditions:Pressure, Temperature, Adsorbent Separation, Membrane Separation, Filter Separation, Centrifugal Separation, Fractional Separation



Case Study #1 –Extraction of Peppermint Oil from Raw Peppermint Leaves

The traditional isolation method for peppermint oil is by steam distillation. SFT developed a process to extract peppermint oil using supercritical fluids. Interestingly enough, the true peppermint "taste"that you are familiar is actually a combination of the pure peppermint oil isolated and the partial thermal decomposition products of the pure peppermint oil. The taste of"pure"peppermint oil is very different from that of the traditional steam distillation method. After determination of the general solubility parameters of peppermint oil in the SFT-Phase Monitor a matrix of extraction conditions were explored. The SFE conditions were optimized to obtain the highest yield, best quality, and purest fraction.

Fraction 1:Peppermint Oil: Pressure 88 Bar, 60 degrees Celsius, 8-10 liters/minute expanded carbon dioxide gas. Yield of 2.0% Peppermint Oil (Pure Peppermint Fraction).

Fraction 2:Peppermint Oil with some Waxes: 150 Bar, 200 degrees Celsius,8-10 Liters/Minute. Yield of 2.5% Peppermint Oil w/Waxes.

Fraction 3:Dark Wax w/Some Peppermint Oil: 250 Bar, 400 degrees Celsius,Yield of 3.0%.

The yield and quality of pure peppermint oil was greater with supercritical fluids than that of traditional steam distillation and there was no thermal decomposition of theoil noted, giving a much purer fraction.

Case Study #2 -Saw Palmetto Extraction Data to Determine Larger Scale Extractor Operation Conditions

Saw Palmetto is a type of palm tree that grows in parts of the southeastern United States. The berry of the saw palmetto plant contains a compound that may reduce the symptoms of benign prostatichyperplasia (BPH), a noncancerousenlargement of the prostate gland. From the 1870s until 1950, saw palmetto was commonly used to treat prostate and other urinary problems. In the United States, saw palmetto is available as a dietary supplement. There are currently 8 supercritical fluid extraction facilities worldwide processing Saw Palmetto. The experimental path again began with a typical parametric Investigation of extraction conditions on Phase Monitor and Lab SFE Unit. The data was compared to that obtained on pilot scale extraction below. Saw Palmetto extracted by the traditional method (solvent) currently costs at $35-45/kg.Supercritical fluid processing cost ~ $0.80-$1.60/lb.

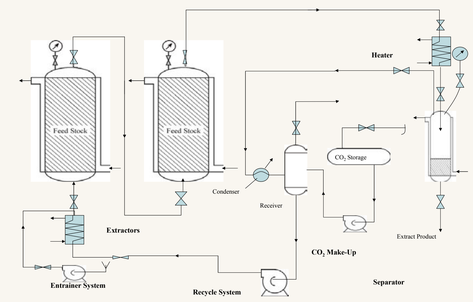
Temp (C)	Pressure (psig)	Solvent/Feed Ratio	Yield (1%)
80	Lquid	10	ND
	3150	30.55	14.46
	5120	18.33	15.13
	8000	18.33	15.07
	9540	18.33	15.27
60	Lquid	10	ND
	3040	27.5	15.6
	5040	18.33	15.13
	7500	18.33	14.86
	9640	18.33	13.33
40	Lquid	10	ND
	3160	27.5	15.86
	5200	18.33	15.27
	7600	18.33	15.6
	9540	18.33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

Saw Palmetto Extraction Data to Determine Extractor Operation Conditions on a Lab Scale Unit

Comparison of Lab Scale and Pilot Plant Results

Pressure	Temp (C)	Lab-Scale SF-Ratio	Lab-Scale Yield (%)	Pilot Plant SF-Ratio	Pilot Plant 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

240 x Scale-Up of Laboratory SFE Data



Saw Palmetto Process Scale Unit

Conclusions: The laboratory scale Phase Equilibrium Monitor and SFE Unit are useful for process development, determining extraction/separation operating conditions. The Variable-Volume Equilibrium View Cell apparatus is an accurate and quick method for obtaining solubility data (especially with multi-component mixtures). The laboratory scale SFE Unit is remarkably accurate for determining extraction rate data for preliminary economic analysis of a Commercial-Scale application. The data obtained matches up well with much larger scale processing units.