Innovations in Supercritical Fluid Technology

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NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

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Innovations in Supercritical Fluid Technology

Supercritical Fluid Applications:

- Solvent replacement
- Extractions
- Drying processes
- Polymerizations
- Environmental applications
- Supercritical water oxidation
- Rapid expansion powder formation

Pharmaceuticals and food processing

Influence on Thrust D- Lithography:

- Similar challenges & limitations

-up of processing

Supercritical Fluid: Environmental Compatibility

Sustainable Development in Technology

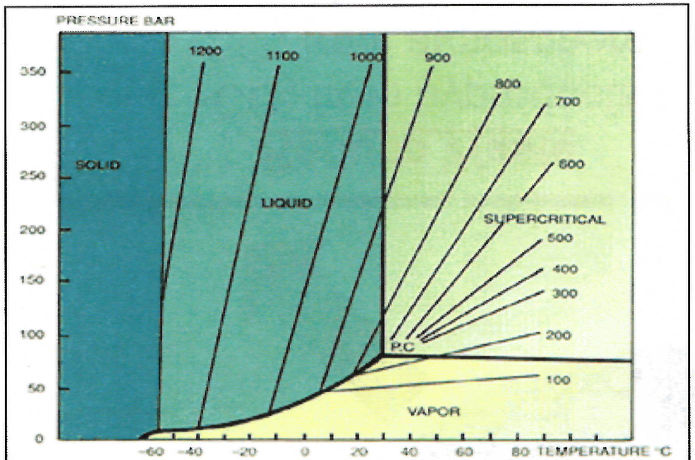
Reduce Waste

- CO_2 from byproducts
- CO_2 from atmosphere
- Reclyclable
- No aqueous waste produced
- Water replaces organic solvents

Reduce Biohazards

- No solvent exposure hazard
- Non-flammable
- Non-toxic
- Water and CO_2

Supercritical Carbon Dioxide



Phase diagram of CO_2. Constant density lines (g/l)

	GAS	Supercritical Fluid		Liquid
	P=0.1 MPa T= 15 °C	Tc, Pc	Tc, 4Pc	P=0.1 MPa T= 15°C
Density ρ (g/cm^2)	0.0006 – 0.002	0.2- 0.5	0.4- 0.9	0.6- 1.6
Viscosity μPa•s	10-30	10-30	30-90	200-3000
Diffusion cm^2/s	0.1- 0.4	0.7×10^{-3}	0.2×10^{-3}	0.2×10^{-5} 2.0×10^{-5}

- High & variable density
- Higher diffusion than liquid
- Viscosity comparable to gas
- Tunable solvating power

Supercritical Fluids

Critical Point:	Tc	Pc
CO_2	31 °C	73.8 atm
Ethanol	240.9 °C	64.1 atm
CO_2 + 7 mol% Et:	52 °C	97 atm
Water	374 °C	220 atm

Disadvantages:

- Elevated pressures required
- Compression costs
- High capital equipment investment

Advantages:

- Controllable dissolving power
- SCF easily recoverable from extract
- Non-toxic solvents, no residues
- Separations not possible by traditional methods can be effected
- Thermally labile compounds can be extracted, low temperature use
- Relatively inexpensive solvents, continuously recycled.

Supercritical Water

Water: Reaction Solvent Affect

ε_{H20} : 78 at STP

ε_{H20} : 2-30 within SCF region (6 at Tc, Pc)

$\varepsilon_{Propane}$: 1.6

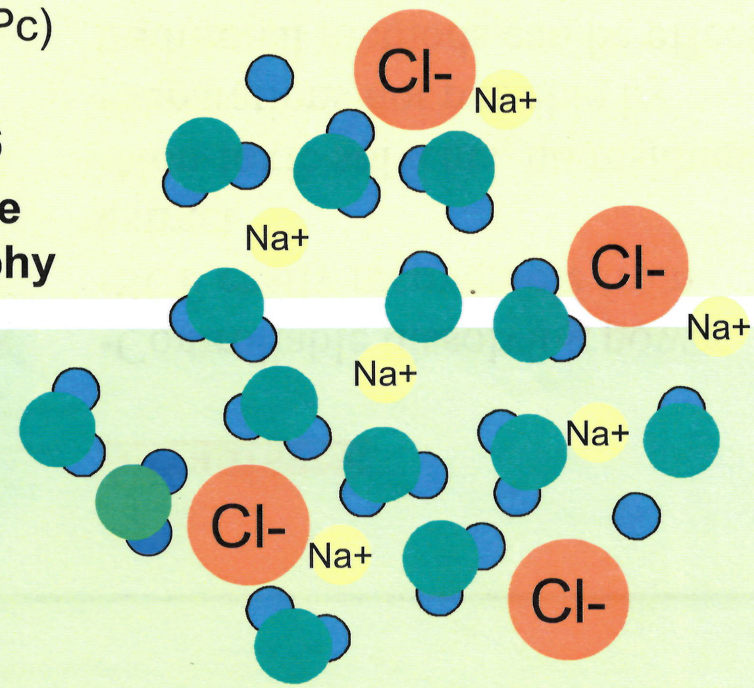
$\varepsilon_{Carbon\ Tetrachloride}$: 2.2

$\varepsilon_{Acetone}$: 20.7

$\varepsilon_{Methanol}$: 32.6

- **Organic substances become soluble**
- **Tunable separations/ chromatography**

SCW: 77% contact ion pairs
H20: 2.6% CIP; 2-6 x more H-bonds
Chialvo: molecular simulations



Water: Ion Product Affect

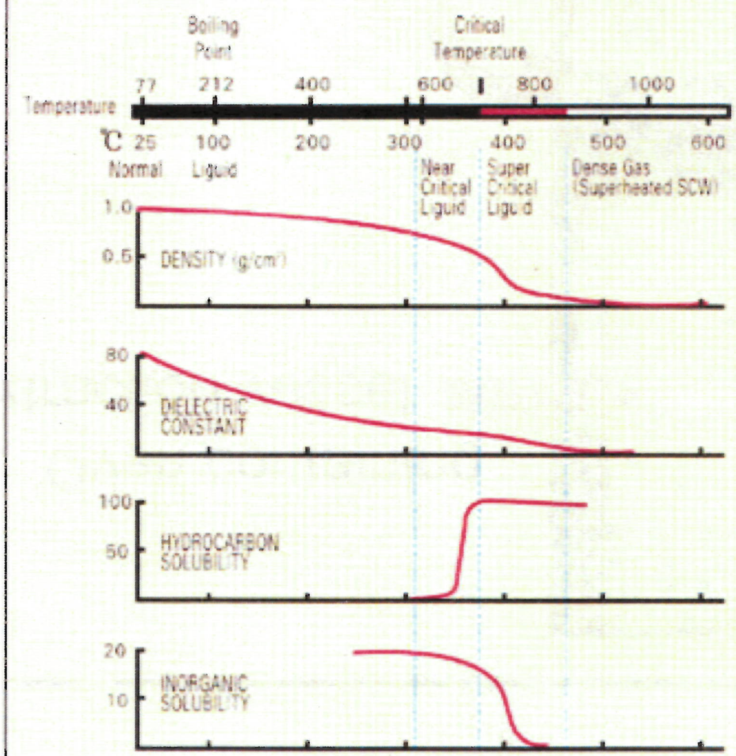
$K_w = [H^+][OH^-]$

$[H^+] = 1x10^{-7}$ at STP

$[H^+] = 3x10^{-6}$ at 300 °C

- **Acid or base catalyst**
- **Electrolyte solvent**
- **Effective Hydrolysis**

Supercritical Water



Properties of water at 250 atm.

Changes occur at SCF transition:

Decrease in Density

Decrease in Dielectric Constant

Increase in Hycrocarbon Solubility

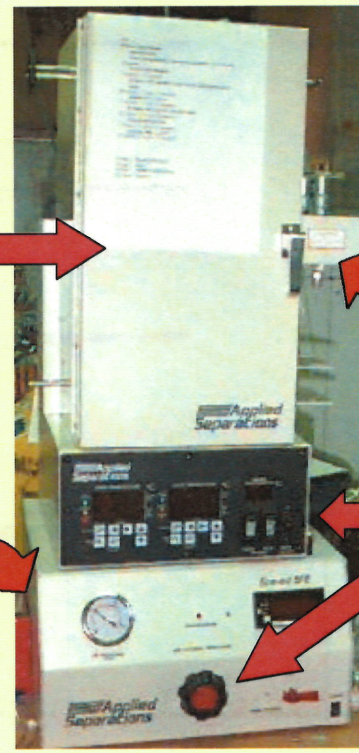
Decrease in Inorganic Solubility

http://www.labkorea.com/products/reactor/

Supercritical Fluid Extraction

4. Oven containing extraction vessel

5. Trapping vessel



http://www.scimedia.com

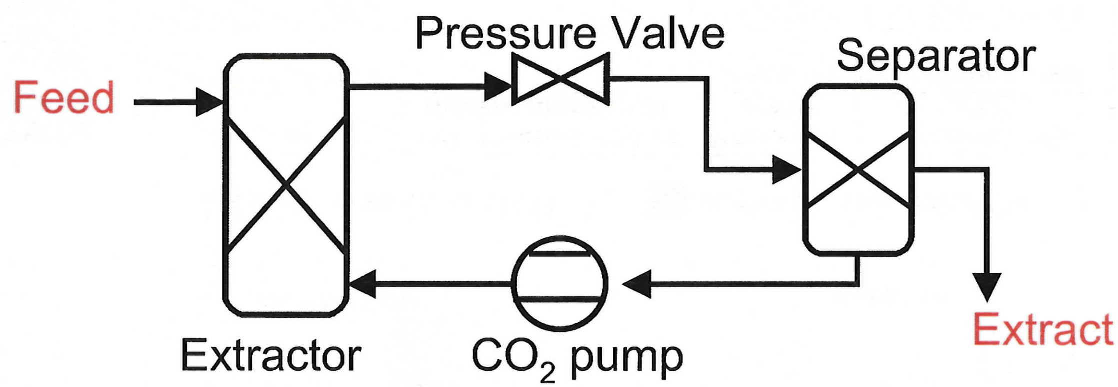
3. Digital Temperature and Pressure control

1. Incoming CO2 mobile phase

2. Pressurizing pump

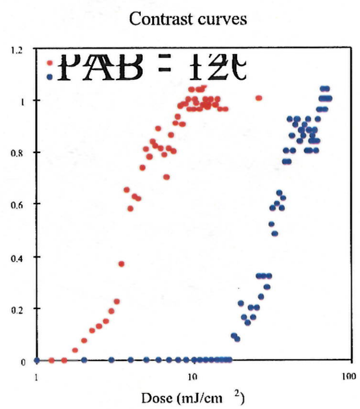
Supercritical Fluid Extraction

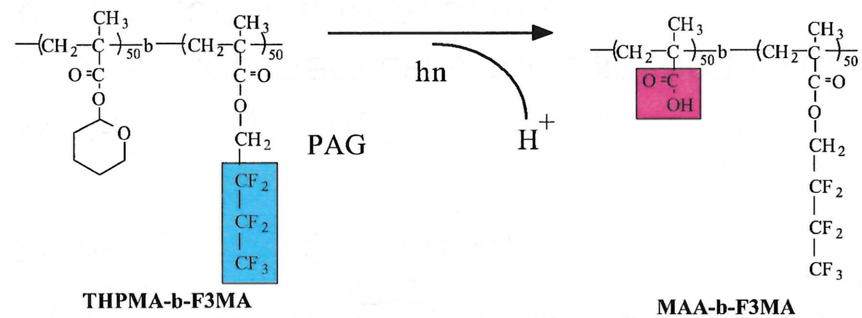
Inexpensive, no solvent residue, non-organic, easy processing control.



- Purification of odorants
- Removal of agrochemicals from ginseng extract.
- Removal of caffeine from coffee
- Removal of water from ethanol.
- Fractionation; removal of monomer from polymer
- CO_2 Dry cleaning to replace carcinogenic PERC

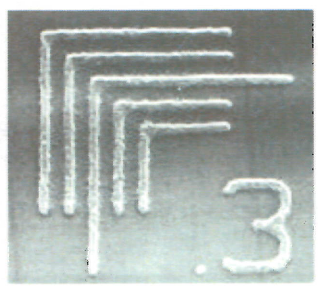
Solvent Replacement: Lithography





soluble in supercritical CO_2 insoluble in supercritical CO_2

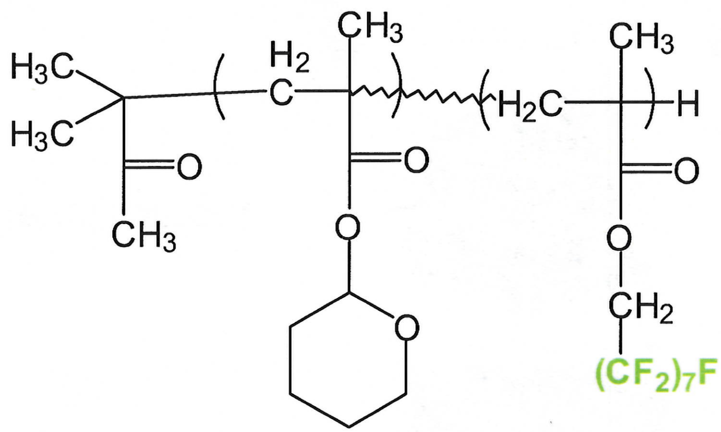
Thickness ~ 2700 Å
Halo alkyl Iodonium PAG ~ 1 wt %
PAB - 120C/60s
PEB - 120C/60s
SCF CO_2 at 45C, 4500 psi



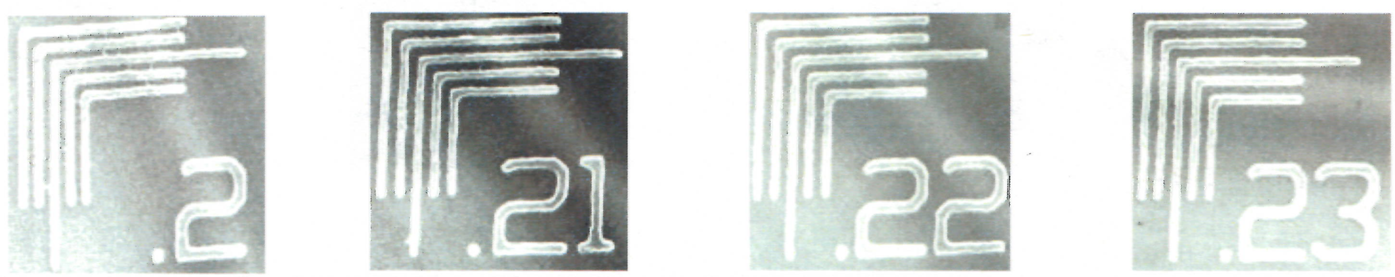
Polymer	Vol. fraction (%) of fluorocomponent	Pressure (psi)	Temperature (°C)
THPMA-b-F3MA	22	Insoluble at conditions tried	
THPMA-b-F3MA	32	Insoluble at conditions tried	
THPMA-b-F3MA	46	Insoluble at conditions tried	
THPMA-b-F3MA	51	4500	45
THPMA-b-F3MA	56	*6500*	*65*
THPMA-b-F3MA	62	2800	45

Narayanan Sundararajan
Cornell University

Solvent Replacement: Lithography



- Block copolymer resist and supercritical development at Cornell
- 193 nm ArF excimer exposure performed at IBM Almaden
- Long image stability (~1 week)



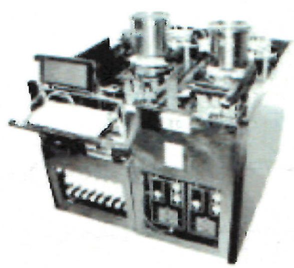
N. Sundararajan, S. Yang, J. Wang, K. Ogino, S. Valiyaveettil, C. K. Ober, S. K. Obendorf and R. D. Allen, "Resists Processed in Supercritical CO_2", *Chem. Mater.*, accepted.

Solvent Replacement
Thrust D: Lithography

Photoresist Application

Semiconductor International, Sept, 1998

Development

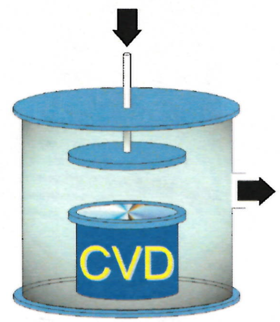


Wet Etch

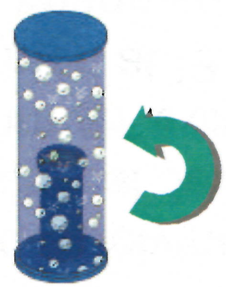
Waste Disposal

VOC Emissions

Solvent Exposure



Gas Effluent Emission



Recyclable Effluent

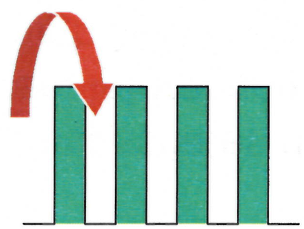
Supercritical CO_2

No net environmental CO_2 increase

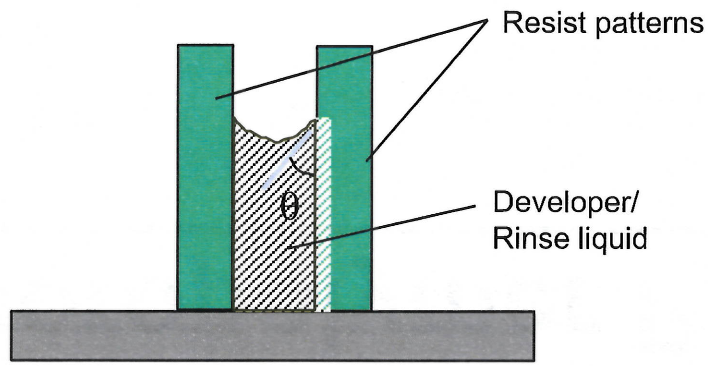
'All Dry' Lithography Process

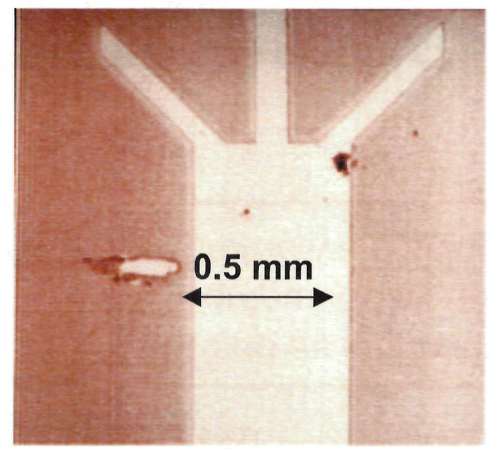
Solvent Replacement
Thrust D: Lithography

High Diffusivity: Enables even development of high aspect ratio features



Low surface tension: Prevents pattern collapse





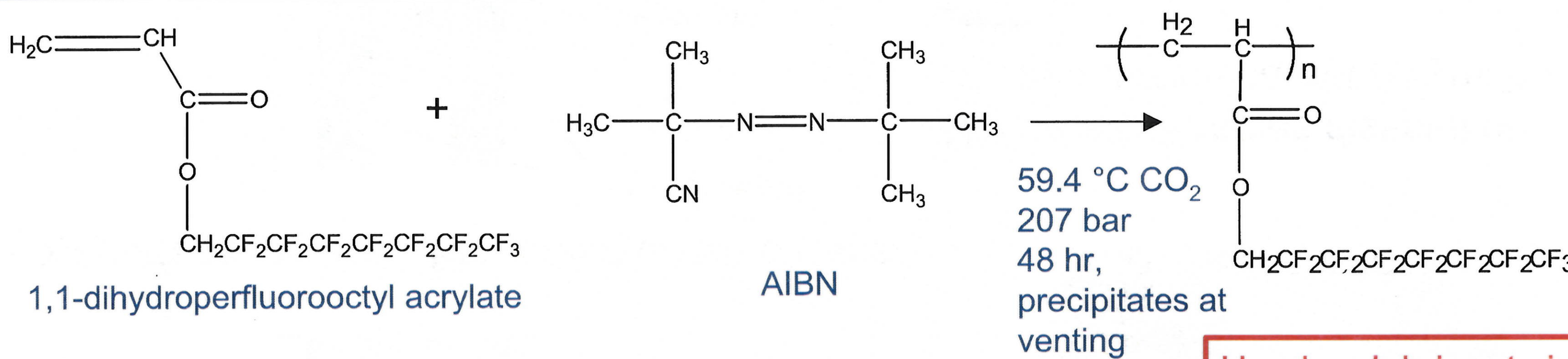
6000 μC/cm^2 CHFPO.HF7

Nonpolar: Enables dissolution of 157nm-transparent polymers

Organosilicon Si:C:O:H

Fluorocarbon $-CF_2-CF_2-$

Solvent Replacement: Fluoropolymer Polymerization



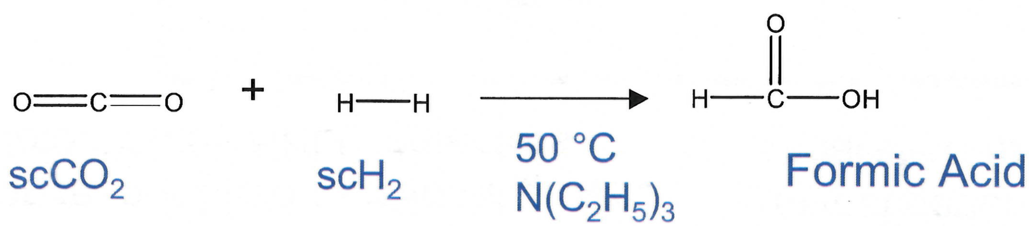
Used as lubricants in computer disk drives, protective coatings.

- Insolubility necessitates use of CFC solvents
- Solute-solvent interaction with F and CO_2 allows 25% solubiltiy of high MW fluoropolymers (>250,000 g/mol)
- Wide range of solvent strengths in SCF by ΔP

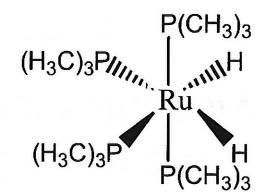
- AIBN composition 2.5 times lower than in benzene (benzene has higher ε)
- Efficiency factor in CO_2 f=0.83, in benzene f=0.53: low viscosity aids diffusion and avoids recombination
- FOA copolymerized with etylene, styrene, MMA, butyl acrylate

DeSimone et al: Science 1992, 257, 945

Other Chemical Reactions: CO_2 as a Reactant



Ru II catalyst complex



- Successful hydrogenation of CO2
- Homogenous catalysis with Ru II complex
- Addition of base to favor product formation
- Product obtained by pressure reduction
- Turnover frequency 1400 h^{-1}; in conventional water 290 h^{-1}

Jessop, Ikarlya, Noyori: Nature 1994, 368, 231

Supercritical Fluid Chromatography (SFC)

HPLC: 2 pumps provide mixed mobile phase, packed column in oven, pressure and flow-rates controlled.

GC: syringe pump & restrictor, flame-ionization detector.

SFC: Higher flow rates
Liquid-like solubility

SFC: Lower Temperatures

- Successful for analytes that won't vaporize, nor have functional groups for detection by HPLC detectors.

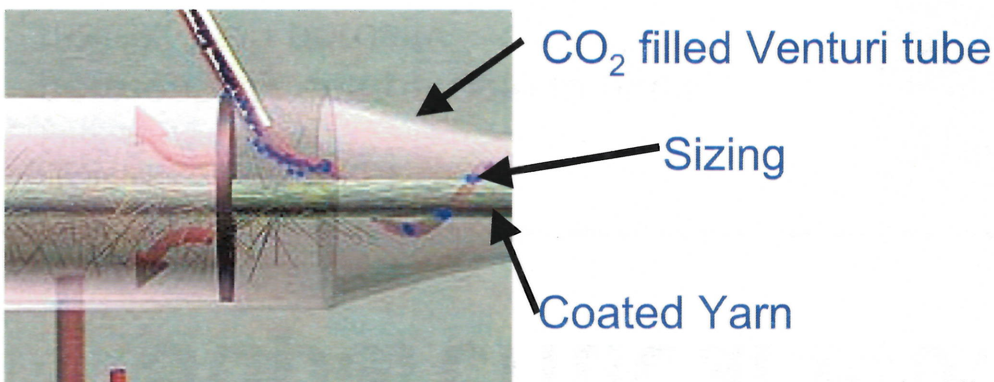
- High resolution & sensitivity.
- Investigation of SFC for enantiomeric separation using chiral stationary phase.

Nicotine and alkaloids in tobacco separated by SFC for analysis.

Polymer Additives

Textile Dyeing & Highly Reflective Material:

- SCF CO_2 infusion of dye to synthetic fibers
- SCF CO_2 infusion of Si containing additive to PEEK
- Rapid CO_2 depressurization leaves additives behind



Textile Sizing:

- Coating a smooth PVA film on fibers to add strength before weaving.
- Adjustment of conditions allows control of penetration.
- Fibers do not stick together after drawing through SCF.

http://scholar.lib.vt.edu/theses/available/etd-93097-173344/

Supercritical Fluid Drying

Silica aerogel :
permeability comparable to glass matrix, high porosity.

Useful as heat or acoustic insulation material

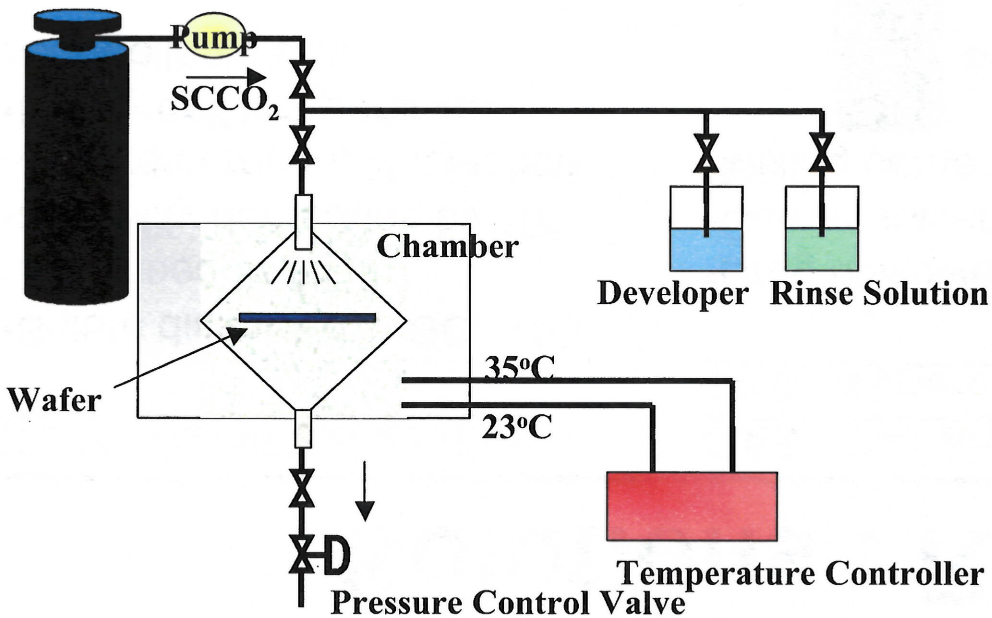
- Drying without vaporization
- No volume expansion from phase change
- No destruction of minute holes in silica gel

- Reactions in CO_2-swollen matrix to create composite materials
- Controlled depressurization renders dense composites
- Rapid pressure quenches yield expanded (microcellular foam) materials.

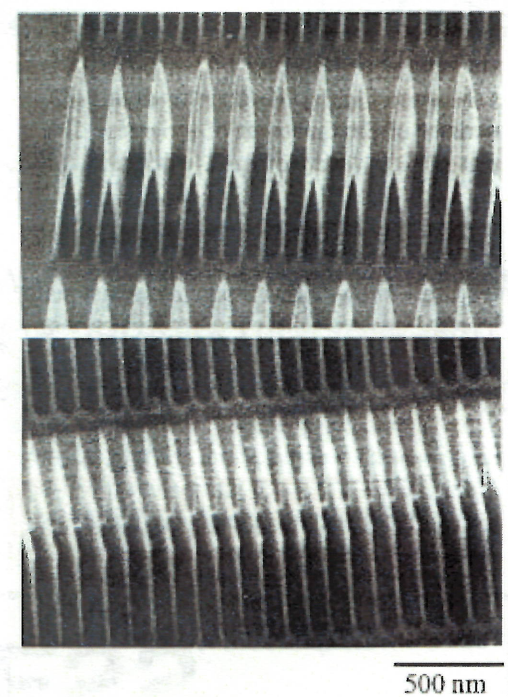
Thomas McCarthy http://www.pse.umass.edu/faculty/mccarthy.html

Supercritical Fluid Drying

- Use CO_2 to replace water or polar solvents.
- Low surface tension avoids capillary forces/ pattern collapse



- N_2 / CO_2 combination used
- Very fine features created

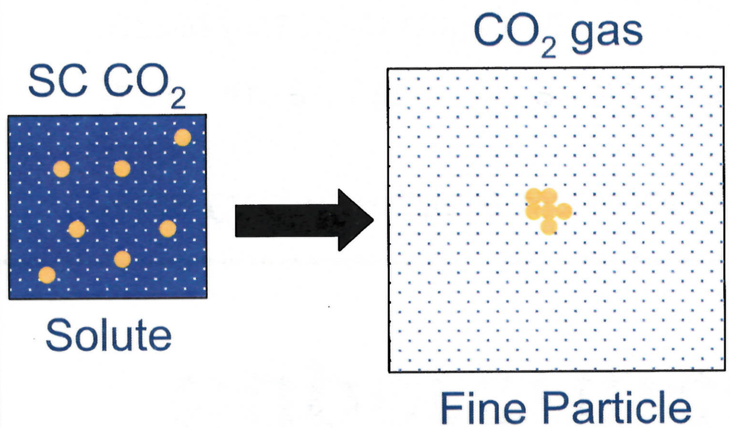


1999 NTT LSI Laboratories, Japan

Rapid Expansion of SCF Solutions : RESS

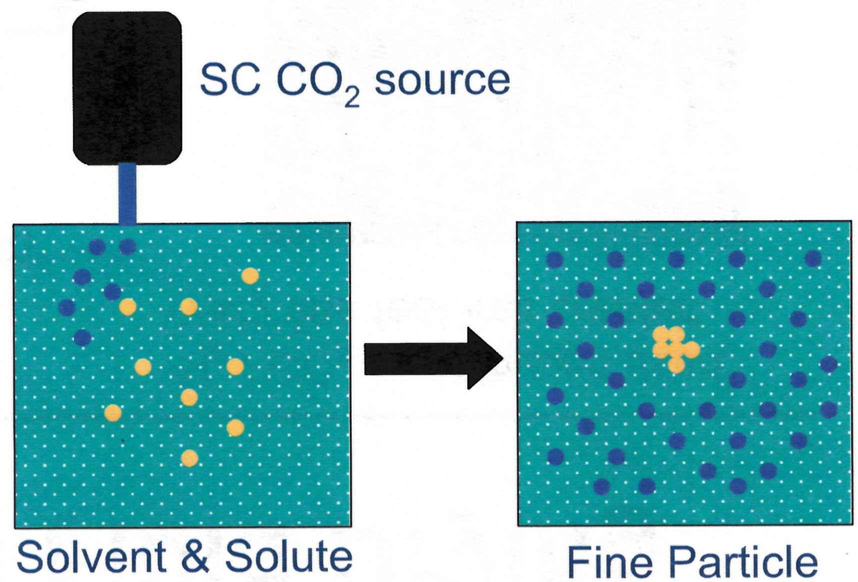
RESS: Rapid Expansion:

- Solute dissolved in SCF CO_2
- Expanded to ATM
- Solubility decreases by 10^6
- Supersaturation, Nucleation
- Highly uniform particles
- Controllable size



GAS: Gas anti-solvent Approach
SAS: Supercritical non-solvent

- Drug dissolves in carrier solvent, not CO_2
- Carrier solvent is partially miscible with CO_2
- Mixing carrier with SCF causes precipitation



RESS/ GAS Applications

Microencapuslation of Flavor and Fragrance: (volatile, themally labile, sensitive to oxidation, expensive)

- Release of flavors during microwaving
- Protection of aspartame during cooking
- Oxidation protection for oils and essences
- Protection during freeze/thaw cycles
- Mask potassium chloride taste
- Reduce flavor mixing: choline and vitamins
- Final product not contaminated with residual solvent
- Process does not degrade active agent as spray drying may

Pharmaceutical Application:

- Aerosol drugs require uniform particles and small size
- Must produce sterile powder
- CO_2 replaces aseptic conditions + use of EtO sterilizer

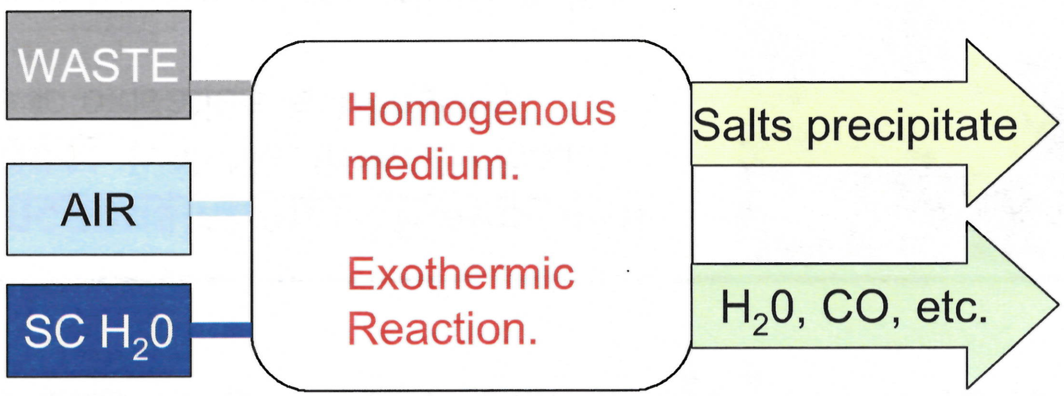
Supercritical Water Oxidation

SCWO: The oxidative destruction of organic wastes in supercritical water.

Above 550 °C toxic organic compounds are miscible, as are oxygen and peroxides in water. Inorganic salts are mostly insoluble.

Destruction of chemical warfare agents, toxic pharmaceuticals

Challenges include: separation of inorganic salts to prevent scaling, & corrosion arising from halogenated hydrocarbons.

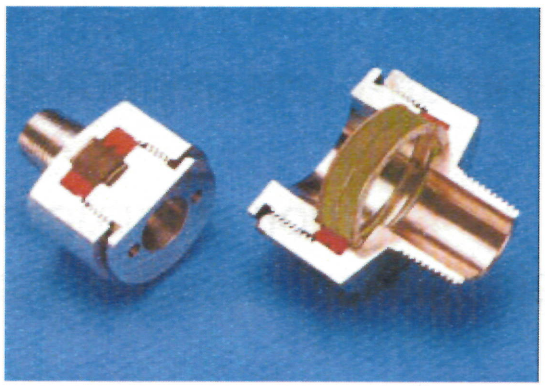


EcoWaste Technologies

Molecular-Level SCF Study

Requirements for Modeling Solubility:

•Properties of all solvents and solutes
•Equation of state: ideal gas, virial, VDW, cubic, Peng-Robinson, etc.
•Temperature dependence, attraction terms, component interaction parameters
•Short and long range (solvation and compressibility driven) effects for solutions



Determine solubility & dissolution behavior in CVD films; interferometery.

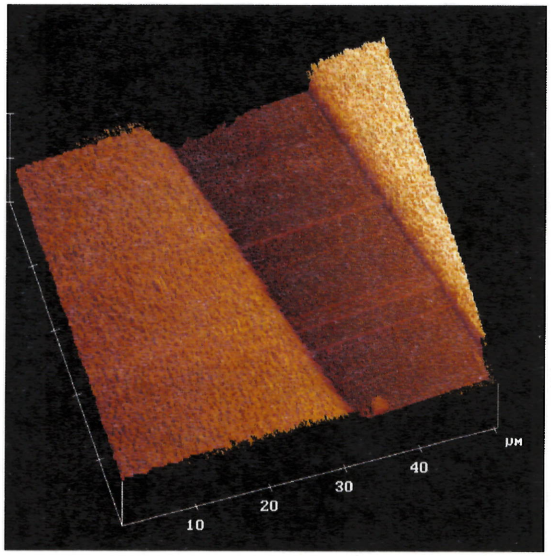
Modeling via regression:

•Based on quantitative structure-property relationships.
•Numerical descriptors may include electrostatic, geometric, and topological parameters, as well as F or other atomic content.

Challenges in SCF Technology

- Feasible designs for scale-up are necessary for commercialization
- Modeling for scale-up not always available/ accurate
- Absence of fundamental, molecular-based model of solutes in SCF
- Continuing instrumental & equipment improvements
- Continuing research & development for applications & new material design

Thrust D: Dry Lithography



AFM/SEM of CHFPO.HF7
Ebeam 6000 $\mu C/cm^2$

- Continuing progress in CO_2 developing of CVD deposited poly(fluoroethers)
- Environmentally benign alternative to aqueous base development
- Useful for patternable low k material
- Aid in resist design for 157 nm laser source or e-beam
- Study to identify structure/property relationships in SCF CO2
- Study of dissolution behavior in films

SRC / NSF

Karen Gleason,
Hilton Pryce Lewis

MIT

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Conclusions

Supercritical Fluids:

•Have unique properties, including high diffusivity, low surface tension, low dielectric constant, and continuously variable density.
•Are non-flammable, non-toxic, inexpensive and do not require special disposal.

Provide alternatives for solvents in cleaning, extraction, and synthesis applications.
•Provide capability for manufacturing specially structured materials, which cannot be produced conventionally.
•Provide new capability for extraction, chromatography, and toxic waste elimination.