Innovations in Supercritical Fluid Technology

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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:

- Awareness of other projects
- Similar challenges & limitations
- Scale-up of processing
- New Opportunities

Supercritical Fluid: Environmental Compatibility

Sustainable Development in Technology

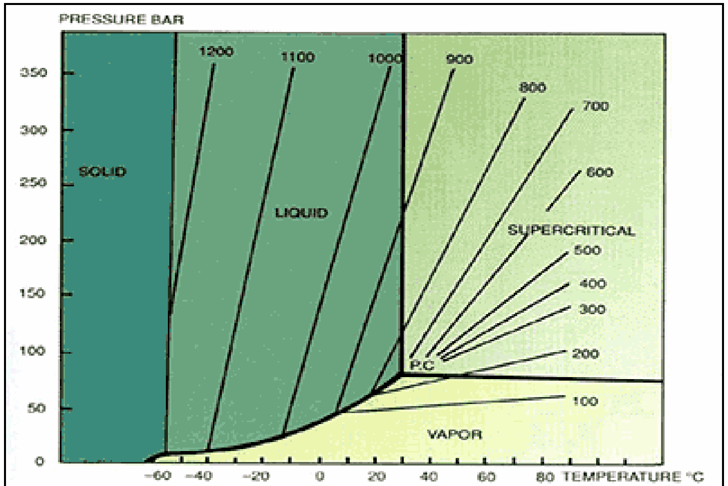
Reduce Waste

- 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

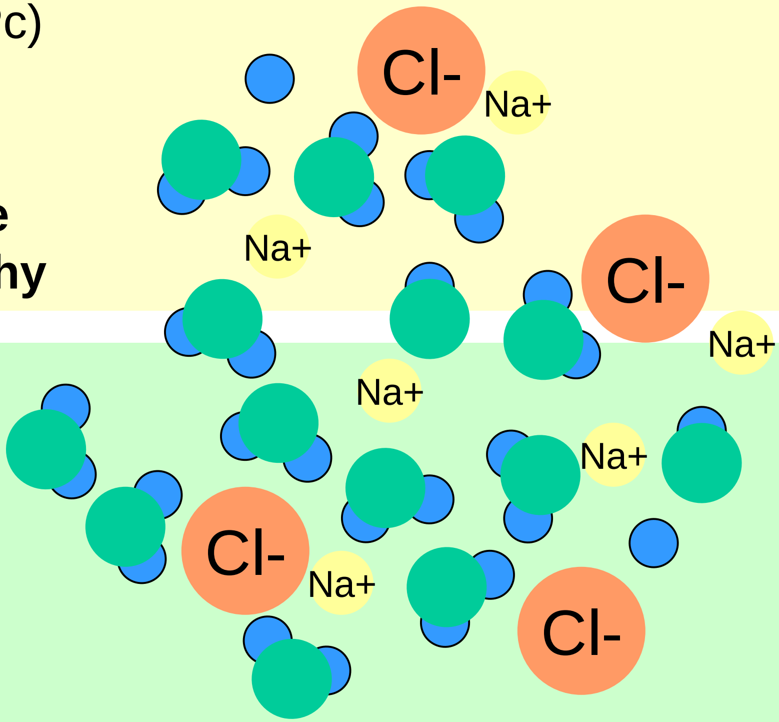
$\varepsilon_{Methanol}$: 32.6

- **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

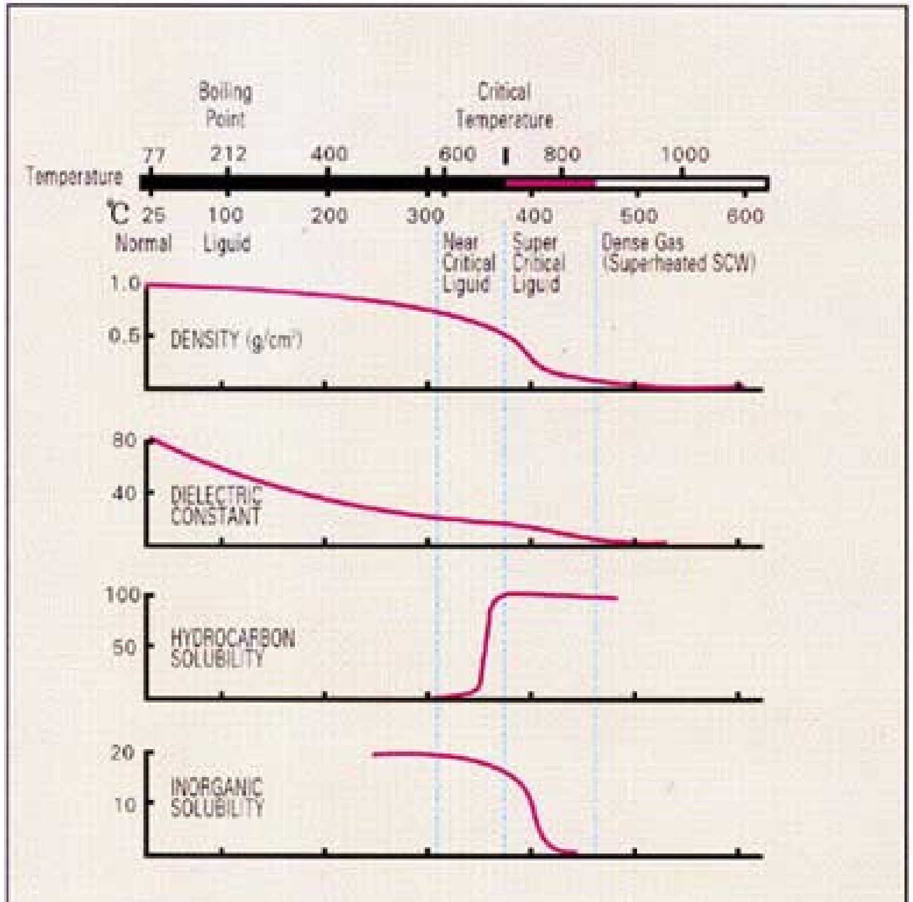
$K_w = [H^+][OH^-]$

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

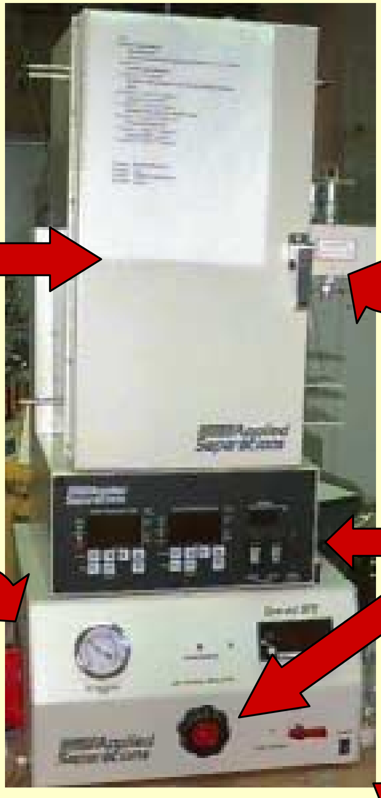
Decrease in Inorganic Solubility

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

Supercritical Fluid Extraction

4. Oven containing extraction vessel

5. Trapping vessel



http://www.scimedia.com

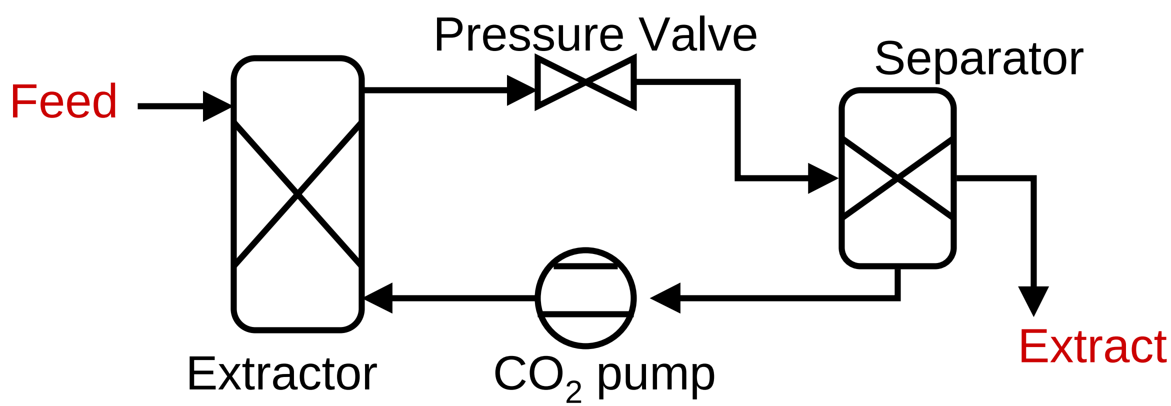
3. Digital Temperature and Pressure control

1. Incoming CO_2 mobile phase

2. Pressurizing pump

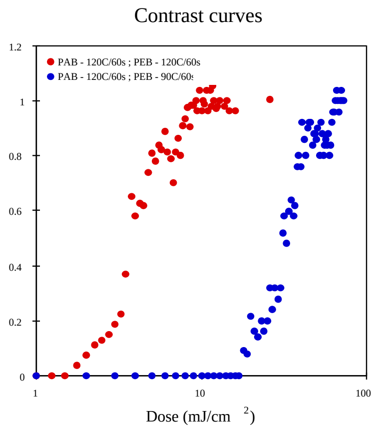
Supercritical Fluid Extraction

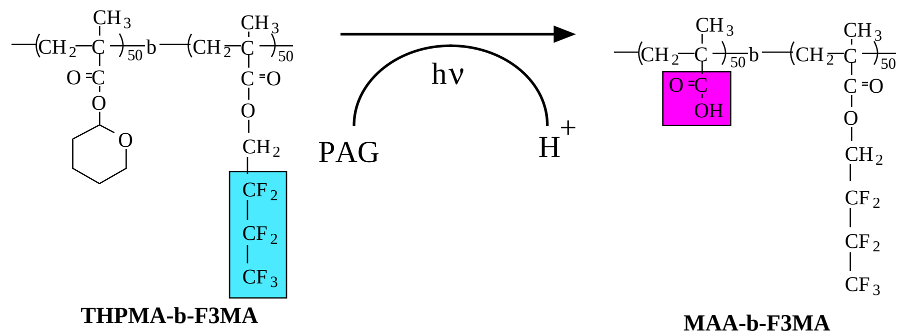
Inexpensive, no solvent residue, non-organic, easy processing control.



- 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

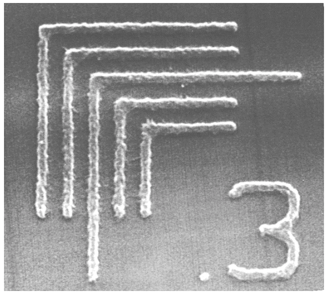
Solvent Replacement: Lithography





soluble in supercritical CO_2 insoluble in supercritical CO_2

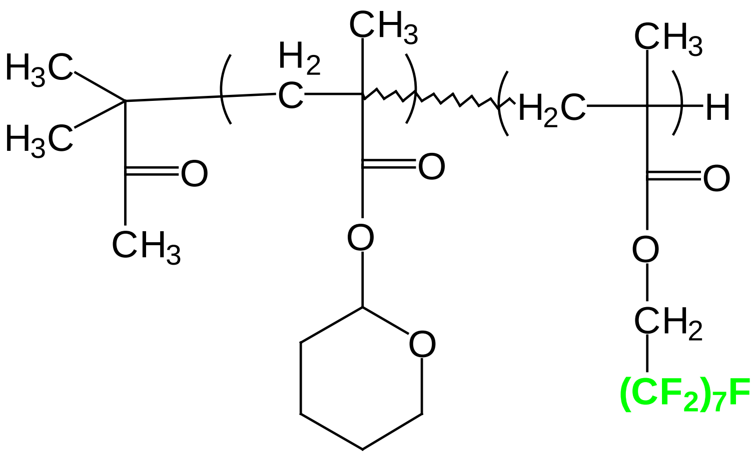
Thickness ~ 2700 Å
Halo alkyl Iodonium PAG ~ 1 wt %
PAB - 120C/60s
PEB - 120C/60s
SCF CO_2 at 45C, 4500 psi



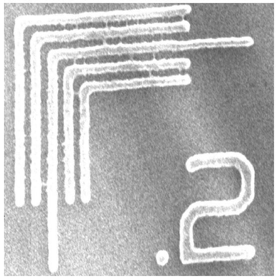
Polymer	Vol. fraction (%) of fluorocomponent	Pressure (psi)	Temperature (^oC)
THPMA-b-F3MA	22	Insoluble at conditions tried	
THPMA-b-F3MA	32	Insoluble at conditions tried	
THPMA-b-F3MA	46	Insoluble at conditions tried	
THPMA-b-F3MA	51	4500	45
THPMA-b-F3MA	56	*6500*	*65*
THPMA-b-F3MA	62	2800	45

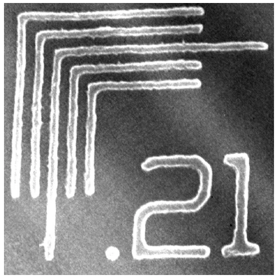
Narayanan Sundararajan
Cornell University

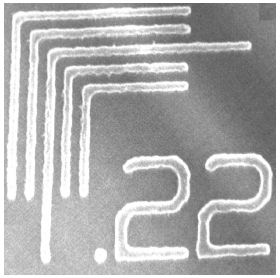
Solvent Replacement: Lithography

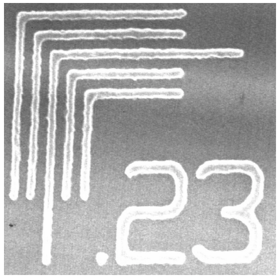


- Block copolymer resist and supercritical development at Cornell
- 193 nm ArF excimer exposure performed at IBM Almaden
- Long image stability (~1 week)





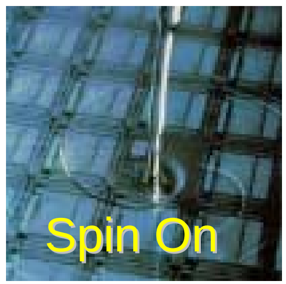




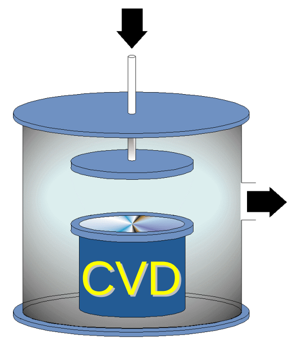
N. Sundararajan, S. Yang, J. Wang, K. Ogino, S. Valiyaveettil, C. K. Ober, S. K. Obendorf and R. D. Allen, "Resists Processed in Supercritical CO_2", *Chem. Mater.*, accepted.

Solvent Replacement
Thrust D: Lithography

Photoresist Application



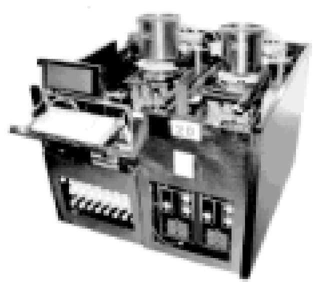
Semiconductor International, Sept, 1998



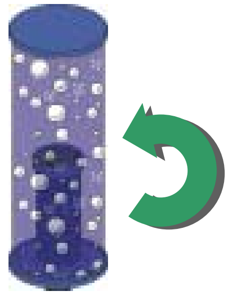
Gas Effluent Emission

'All Dry' Lithography Process

Development



Wet Etch



Recyclable Effluent

Supercritical CO_2

Waste Disposal

VOC Emissions

Solvent Exposure

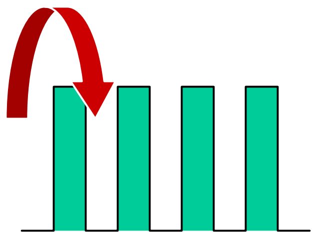
No net environmental CO_2 increase

NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing

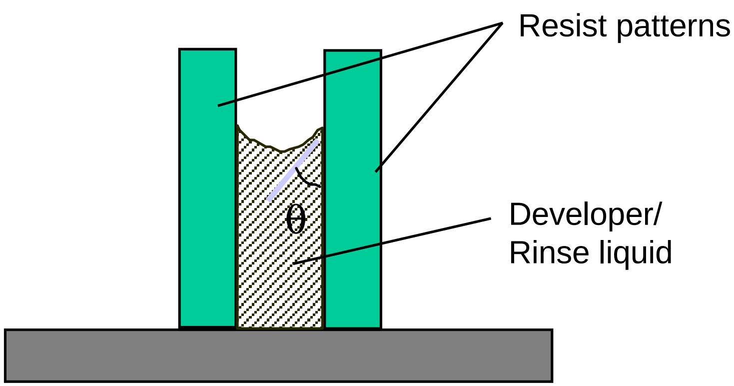
CORNELL UNIVERSITY

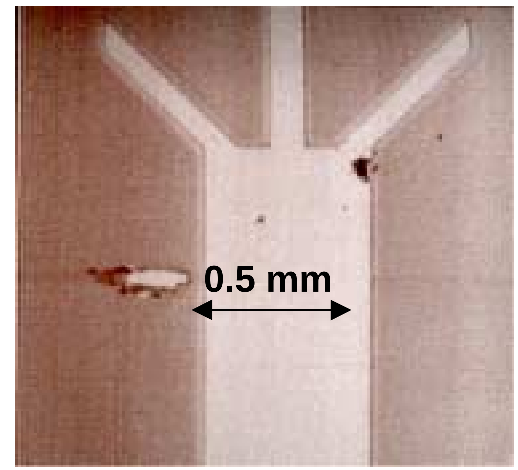
Solvent Replacement
Thrust D: Lithography

High Diffusivity: Enables even development of high aspect ratio features



Low surface tension: Prevents pattern collapse





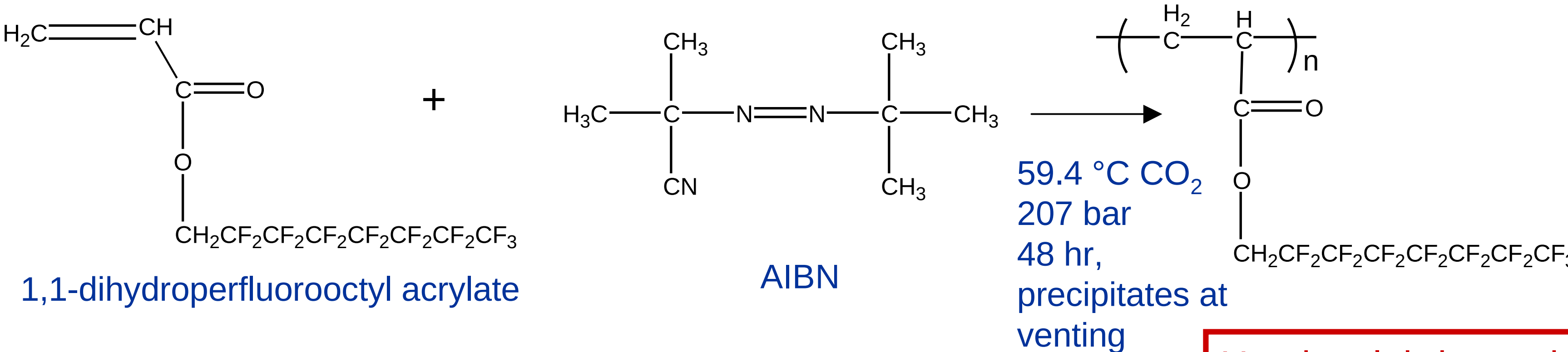
6000 µC/cm² CHFPO.HF7

Nonpolar: Enables dissolution of 157nm-transparent polymers

Organosilicon
Si:C:O:H

Fluorocarbon
$-CF_2-CF_2-$

Solvent Replacement: Fluoropolymer Polymerization



1,1-dihydroperfluorooctyl acrylate

AIBN

Used as lubricants in computer disk drives, protective coatings.

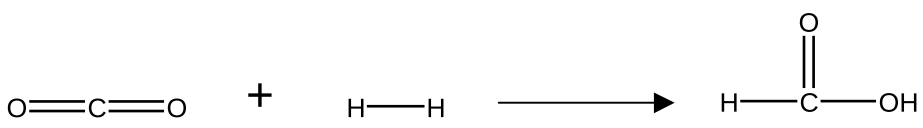
- Insolubility necessitates use of CFC solvents
- Solute-solvent interaction with F and CO_2 allows 25% solubiltiy of high MW fluoropolymers (>250,000 g/mol)
- Wide range of solvent strengths in SCF by ΔP

- 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

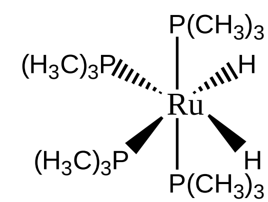
DeSimone et al: Science 1992, 257, 945

Other Chemical Reactions: CO_2 as a Reactant

Ru II catalyst complex



$scCO_2$ scH_2 50 °C $N(C_2H_5)_3$ Formic Acid



- 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.