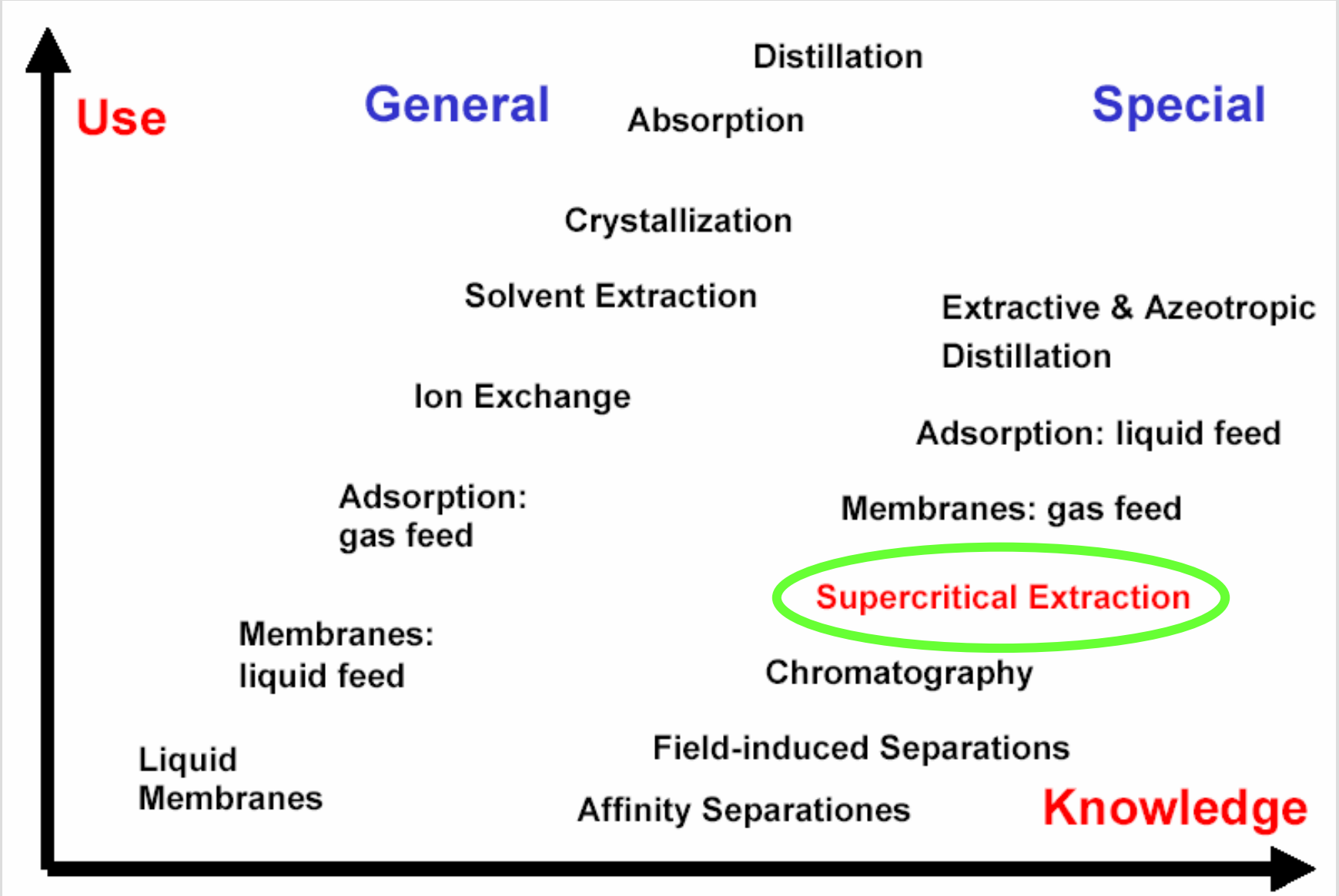
TEHNICI DE SEPARARE SI CONCENTRARE IN BIOTEHNOLOGII

EXTRACTIA CU FLUIDE SUPERCRITICE

Procese de separare

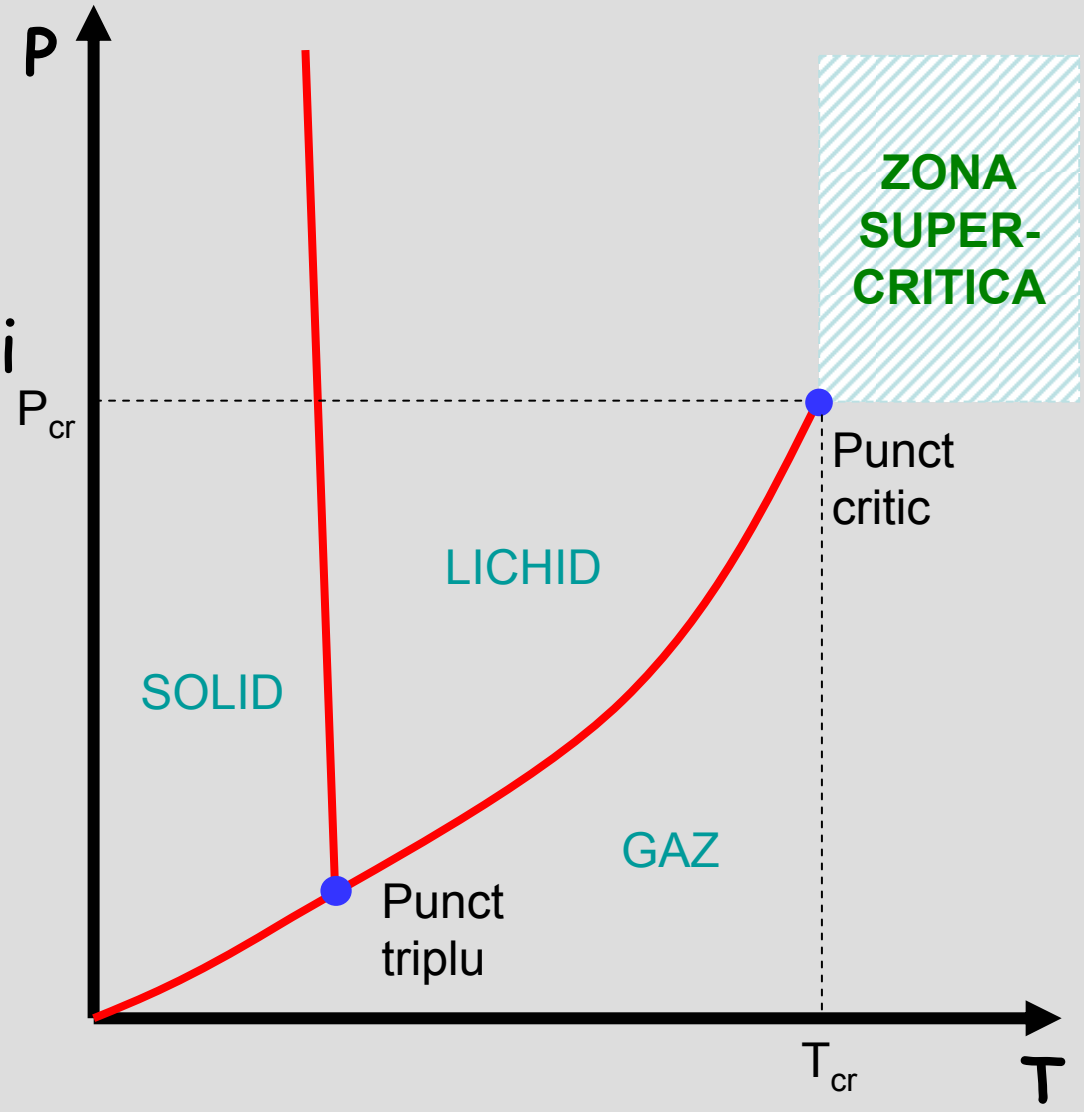


ISTORIC

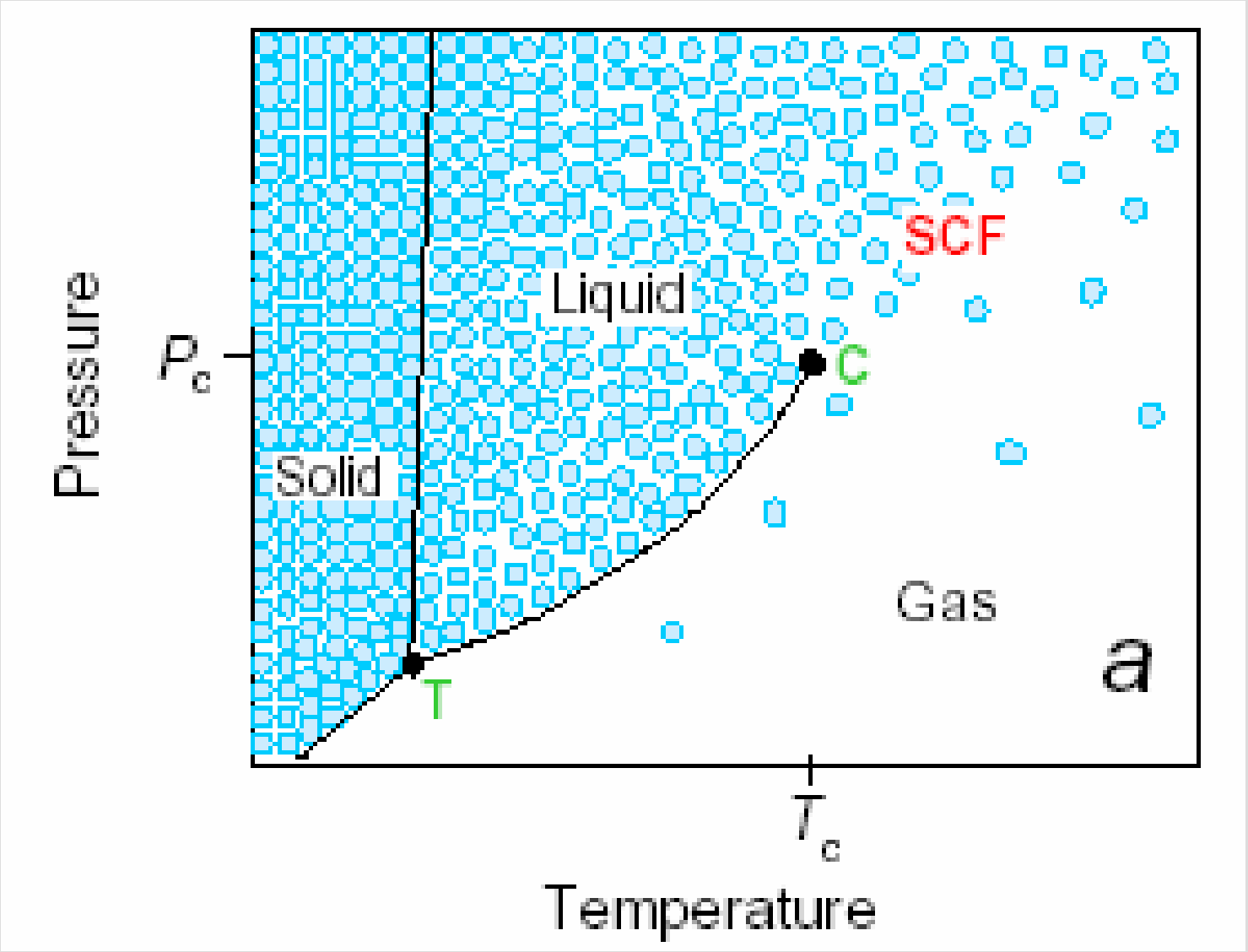
- Cunoscuta de 125 de ani (Hannay & Hogarth, 1879 – The Royal Society of London);
- Ignorata pana dupa cel de-al 2-lea razboi mondial;
- Ia amploare dupa 1971 (Paul & Wise – prevad aplicatii ulterioare in ind. alimentara, farmacie, chimie fina);
- 1979 – prima instalatie ind. de extractie cu CO_2 SC – decafeinizarea cafelei (SUA).

Starea supercritica

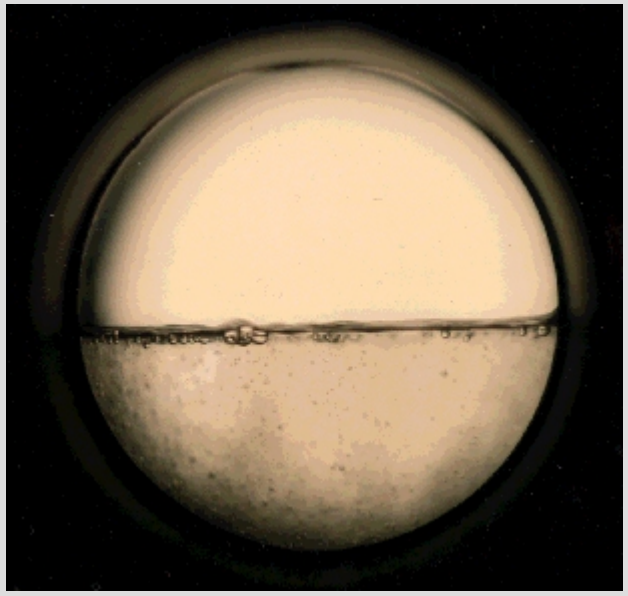
- Diagrama P-T (diagrama de faze)
- Punct triplu:
  - coexista cele trei stari: L, S, G
- Punct critic:
  - diferentele intre L si G dispar
  - proprietatile G sunt identice cu proprietatile L



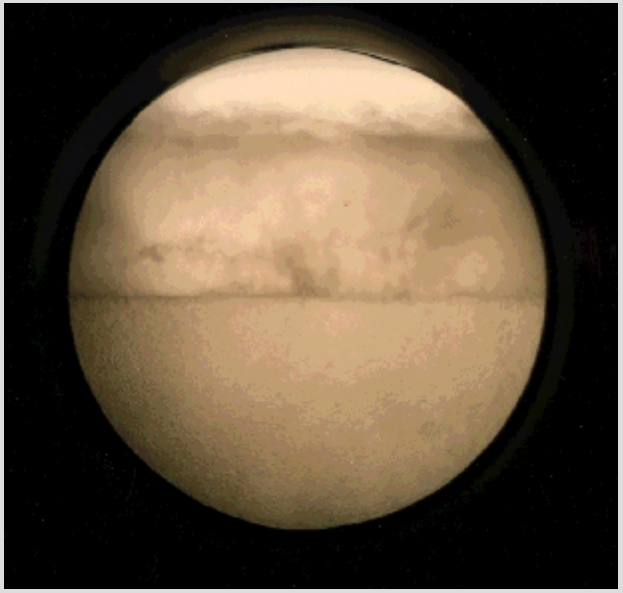
Starea supercritica



Starea supercritica

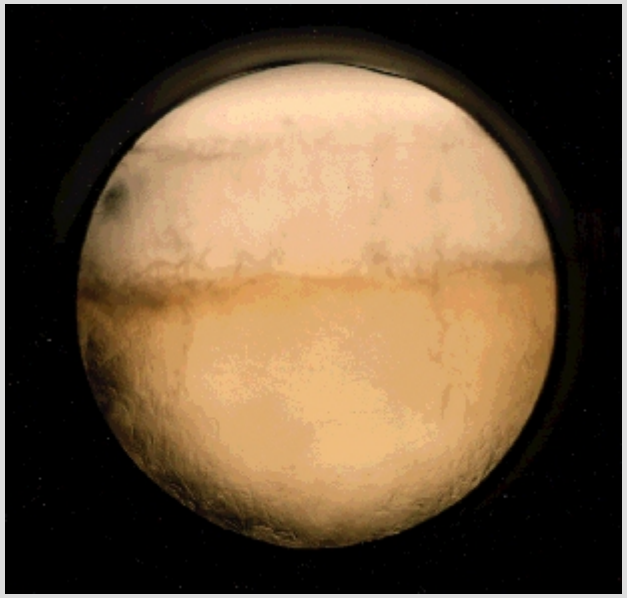


- Menisc vizibil care separa faza lichida (jos) de faza gazoasa (sus)

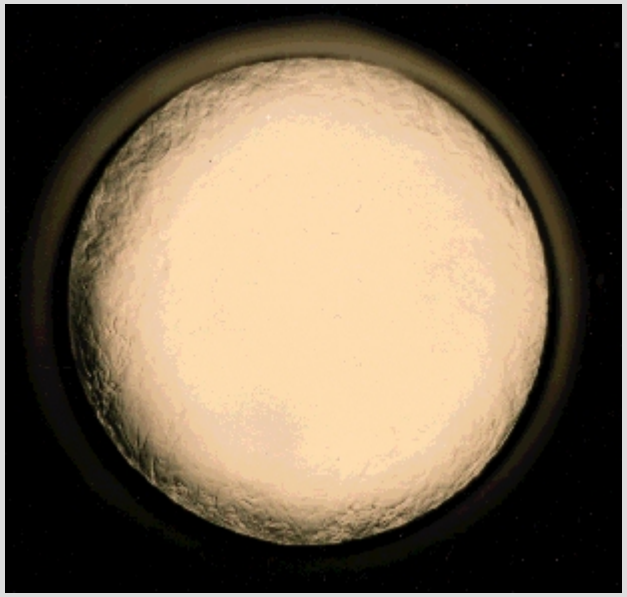


- La cresterea T meniscul se estompeaza

Starea supercritica

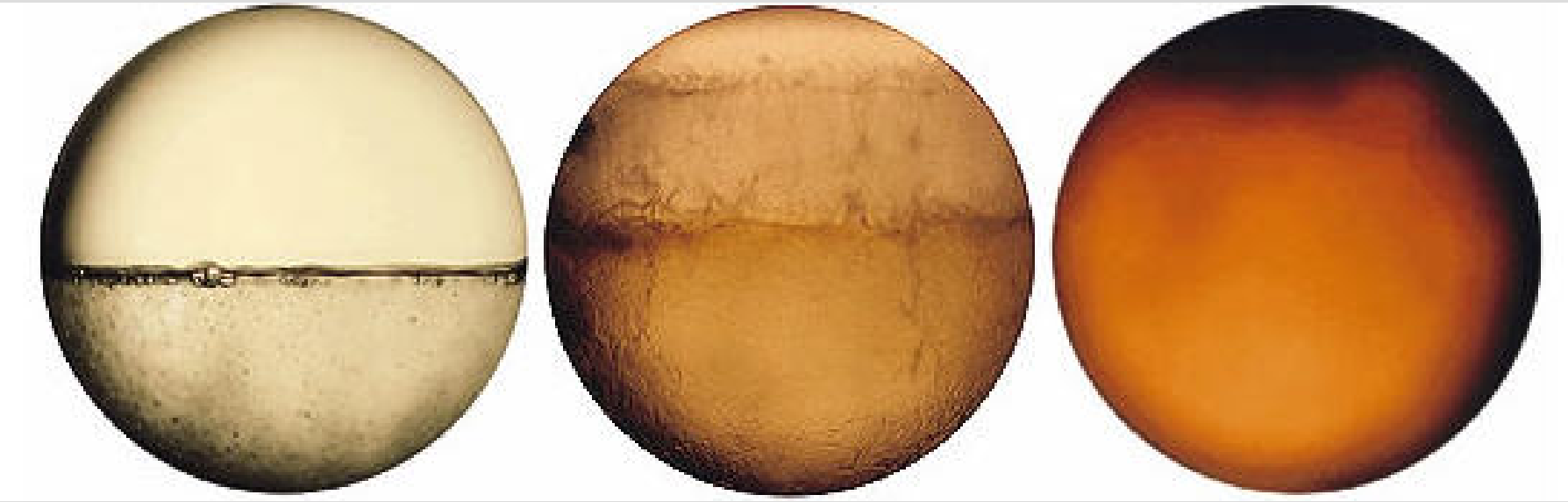


- Cresterea P si T duce la apropierea valorilor ρ_L si ρ_G; meniscul este inca vizibil



- La P_{cr} si T_{cr} meniscul dispare, $\rho_L = \rho_G$;
- Exista o singura faza omogena, **fluidul supercritic (FSC)**

Starea supercritica

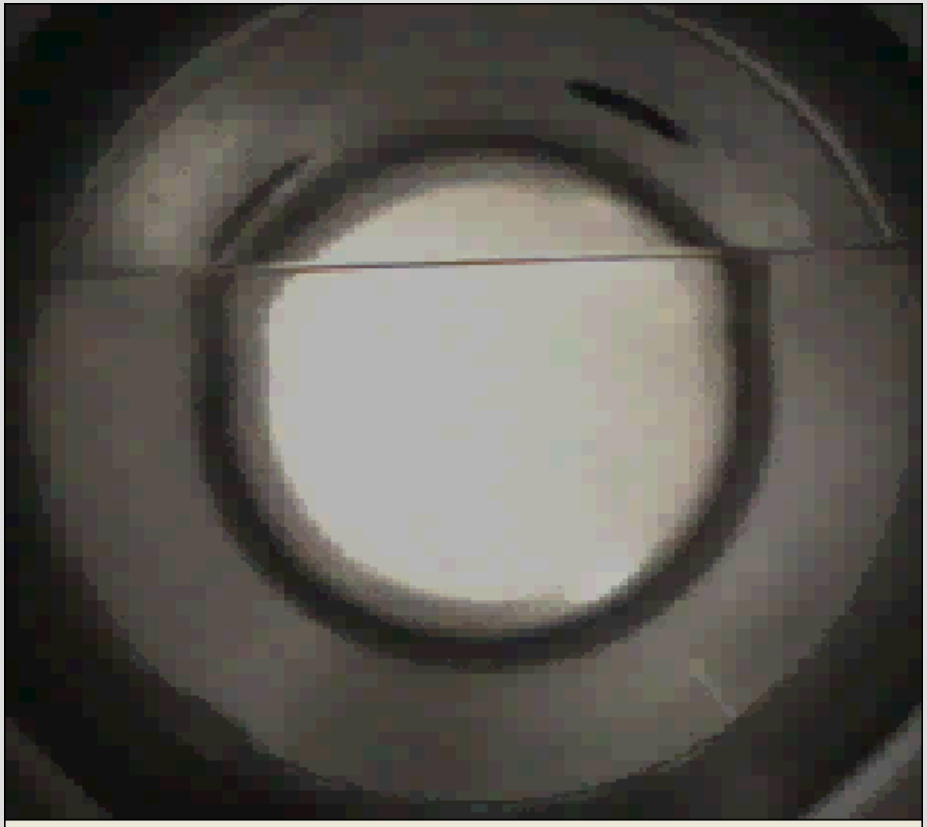


Doua faze distincte
lichid si gaz

Distinctia intre faze
se estompeaza

O singura faza, cea de
FLUID SUPERCRITIC

Starea supercritica



co2vid[1]

Starea supercritica

- In comparatie cu solventii lichizi, **fluidele supercritice** prezinta:
  - difuzivitate ridicata;
  - densitate scazuta;
  - viscozitate scazuta;

  → extractie rapida; separare usoara a fazelor

- Sistemele supercritice combina calitatile L si G, rezultand un fluid foarte "elastic", un solvent cu "geometrie variabila".

Starea supercritica

- Proprietati de transport (Hann, 1991):

Fluidul	Densitate [kg/m^3]	Viscozitate [Pa.s]	Coef. de difuziune [m^2/s]
Gaz: 0,1 MPa 288 - 303 K	0,1 - 2	(1-3).10^{-5}	(0,1-0,4).10^{-4}
FSC: Tcr, Pcr	200 - 500	(1-3).10^{-5}	0,7.10^{-7}
FSC: Tcr, 4Pcr	400 - 900	(3-9).10^{-5}	0,2.10^{-7}
Lichid: 0,1 MPa 288 - 303 K	600 - 1600	(0,2-3).10^{-3}	(0,2-2).10^{-9}

Parametrii critici ai unor posibili solventi

Substanța	Temperatura critică, T_{cr}, K	Presiunea critică, p_{cr}, MPa	Densitatea critică, ρ_{cr}, g/cm^3
Metan	191	4.60	0.162
Etenă	282	5.03	0.218
Clor-trifluorometan	302	3.92	0.579
Dioxid de carbon	304	7.38	0.468
Etan	305	4.88	0.203
Propenă	365	4.62	0.233
Propan	370	4.24	0.217
Amoniac	406	11.3	0.235
Eter etilic	467	3.64	0.265
n-Pentan	470	3.37	0.237
Acetonă	508	4.70	0.278
Metanol	513	8.09	0.272
Benzen	562	4.89	0.302
Toluen	592	4.11	0.292
Piridină	620	5.63	0.312
Apă	647	22.0	0.322

Solventi recomandati

- **Directiva EC 84/344/EEC:**
  - solventi de extractie acceptabili conform cu GMP

Propane	Ethanol
Butane	Carbon Dioxide
Butylacetate	Acetone
Ethylacetate	Nitrous Oxide

Nitrogen, Water

Mixtures

Solventi supercritici

- Solventii cei mai utilizati:

SOLVENTUL	T_{cr} [K]	P_{cr} [MPa]	ρ_{cr} [kg/m^3]
ETENA	282 (9 °C)	5,03 (~50 bari)	0,218
DIOXIDUL DE CARBON	304 (31 °C)	7,38 (~73 bari)	0,468

Solventi supercritici

- Avantajele etenei si dioxidului de carbon:
  - T_{cr} apropiata de T ambianta;
  - P_{cr} nu prea ridicata;
  - solubilitatea ridicata a multor substante in acesti doi solventi;
  - selectivitate buna, care poate fi marita prin adaos de agenti de antrenare;
  - accesibili si cu pret de cost relativ mic;
  - mai putin toxici si periculosi decat alti solventi.

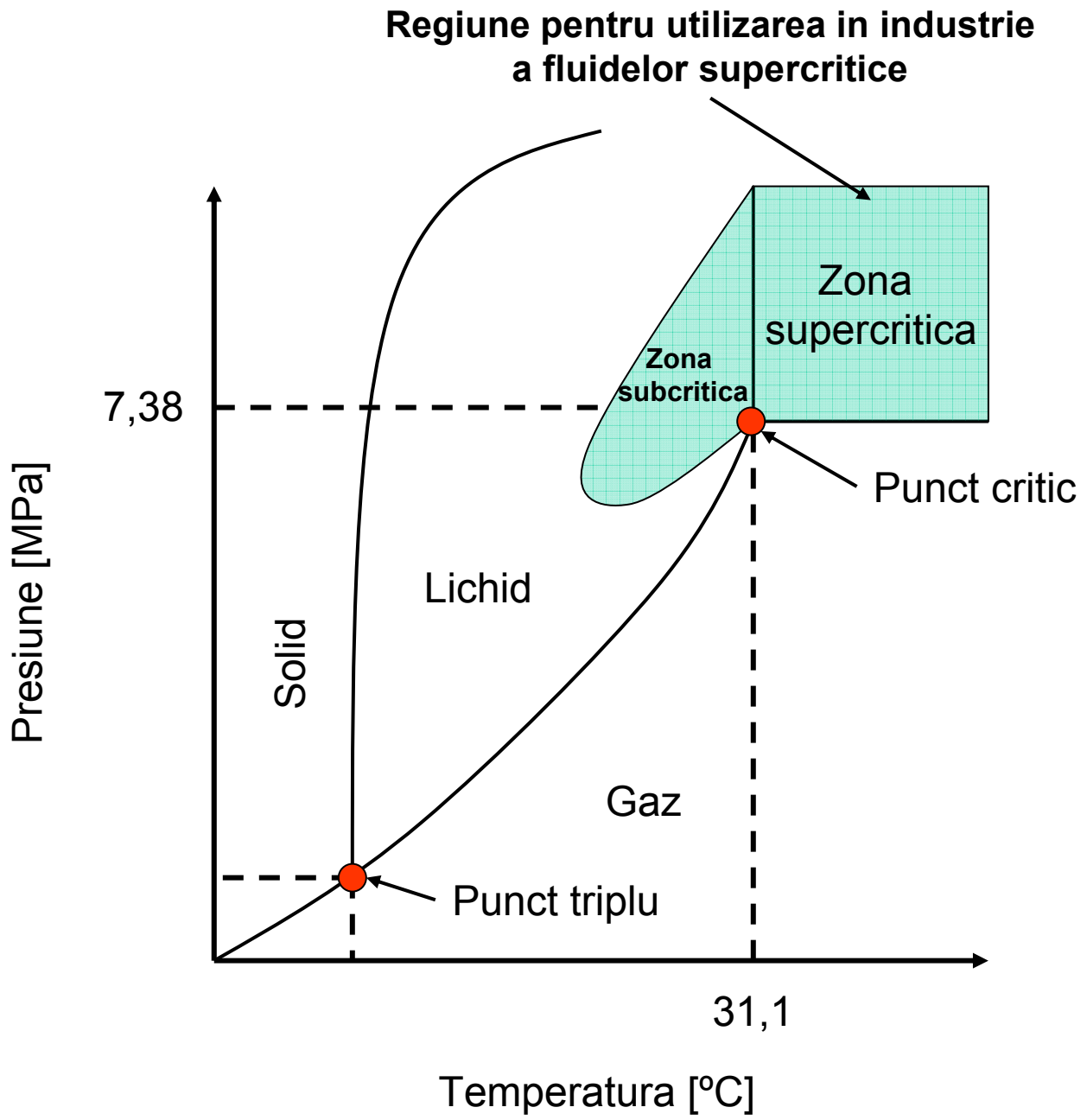
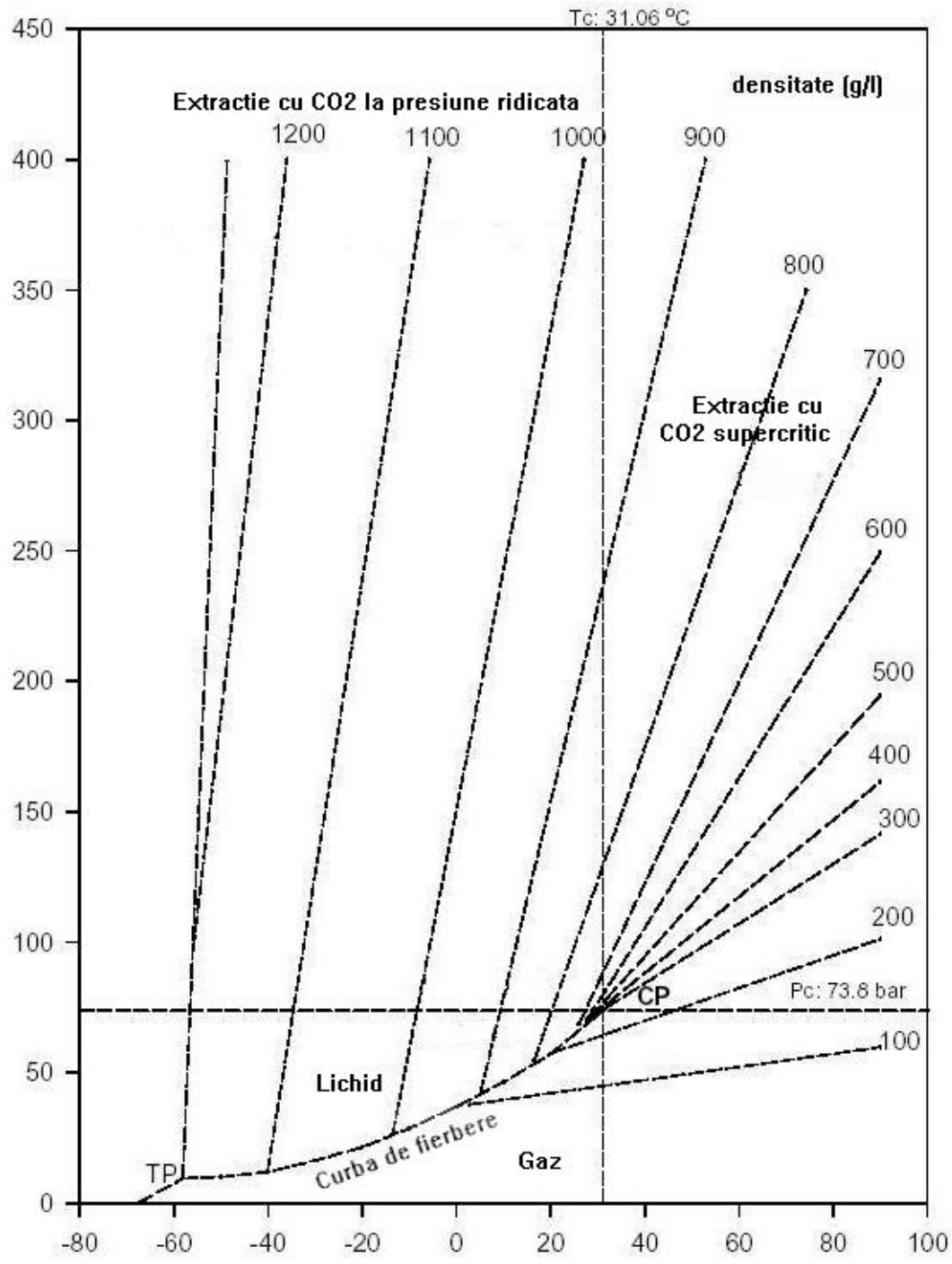
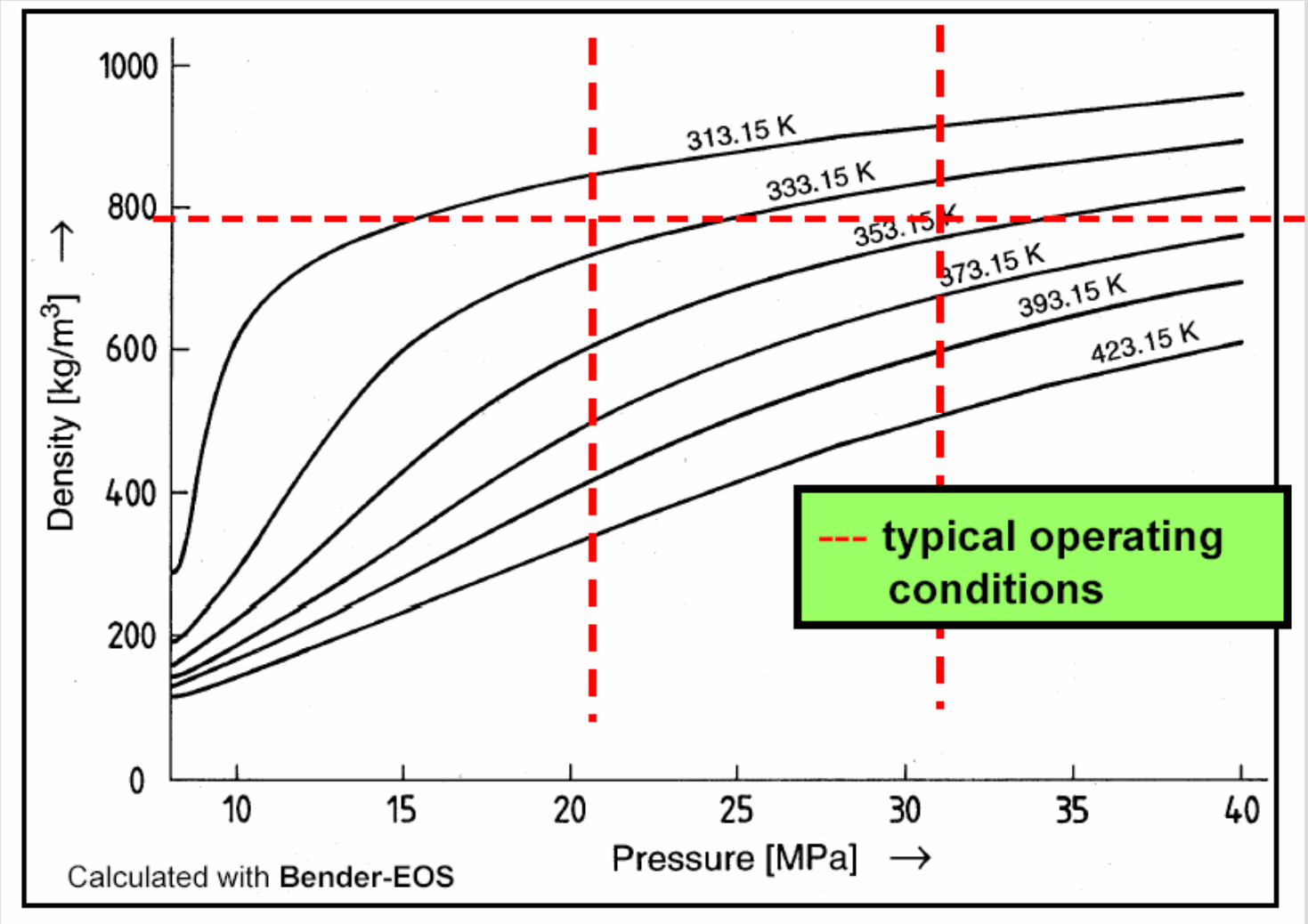


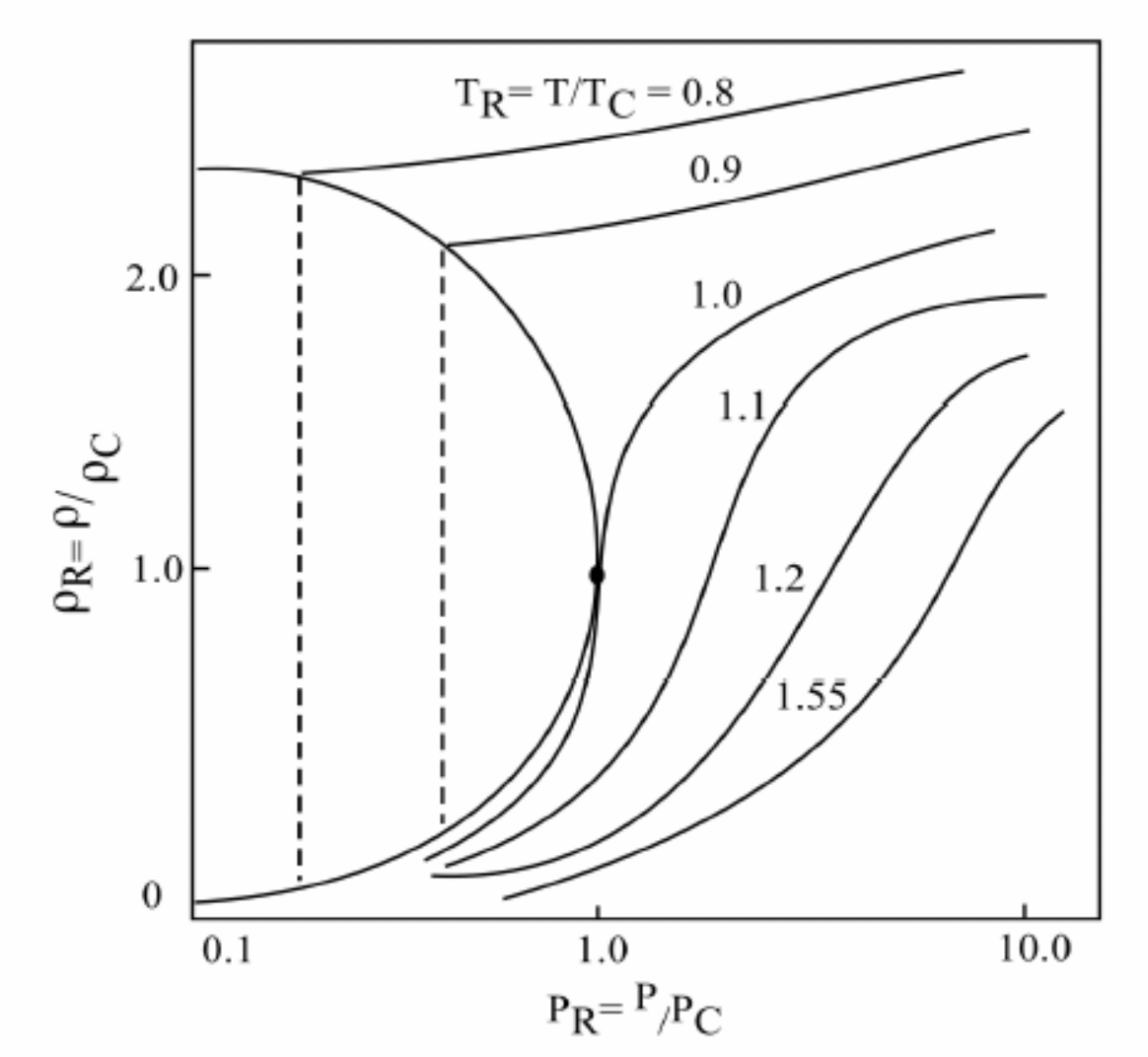
Diagrama de faze a CO_2

- In jurul pct. critic, modificari mici ale P si T conduc la variatii substantiale ale ρ.
- Puterea de solvatare = f(ρ) ➔ solubilitatea creste cu cresterea ρ;
- Extractia = la ρ mari;
- Separarea solutului = la ρ mici



Variatia densitatii CO_2 cu P si T





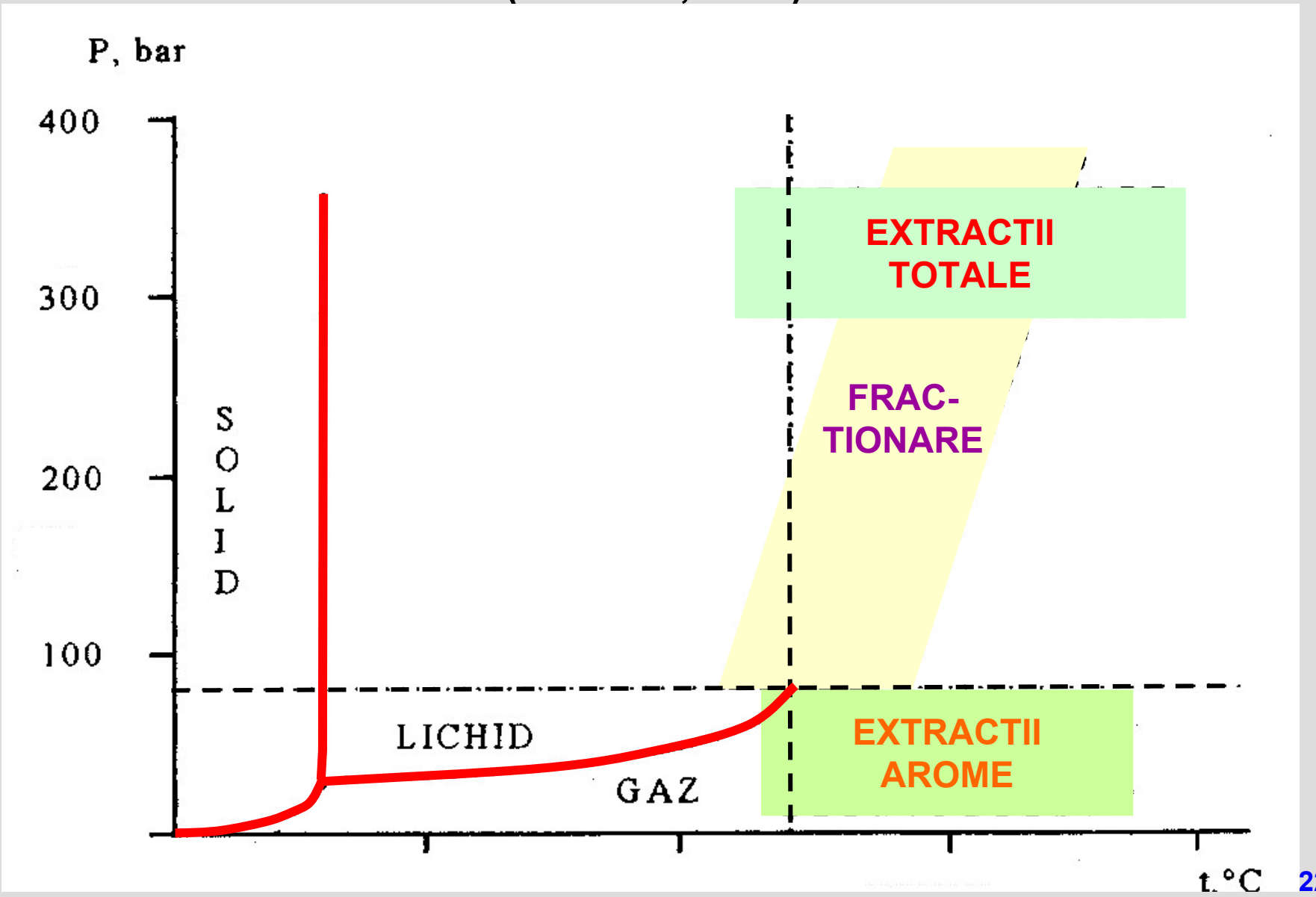
The most useful extraction region is that in which the relative pressure ($P_R = P/P_C$) ranges from 1.01-1.5 and the relative critical temperature ($T_R = T/T_C$) ranges from 1.01-1.1 (Brenneck and Eckert, 1989).

Zone optime de lucru cu CO_2

- Obtinerea de extracte cu compozitii variabile: modificarea puterii de solvatare a CO_2 (P, T, cosolvent, cond. de separare)
  - **Extractie totala:** CO_2 L sau SC la valori ridicate;
  - **Extractie selectiva:** CO_2 G sau SC la valori scazute;
  - **Extractie fractionata:** CO_2 SC la valori succesive diferite de P si T.

Zone optime de lucru cu CO_2

(Brennan, 1990)



Solubilitatea unor compusi in CO_2 lichid la 298 K (Mc Hugh, 1986)

Compuşi	Solubilitate %	Compuşi	Solubilitate %
Esteri		***Amine, heterociclici***	
Benzilbenzoat	10	Anilină	3
Butilbenzoat	M*	o-cloranilină	5
Butilftalat	8	Difenilamină	1
Butilstearat	3	N-etilanilină	13
Etilacetat	M	N-metilanilină	20
Etibenzoat	M	Piridină	M
Alcooli		***Fenoli***	
Alcool amilic	M	o-clorfenol	M
Alcool benzilic	8	p-clorfenol	8
Ciclohexanol	4	o-crezol	2
Alcool metilic	M	p-etilfenol	1
Alcool etilic	M	o-nitrofenol	3
Furfurol	4	Fenol	3
Acizi carboxilixi		***Nitrili şi amide***	
Acid acetic	M	Acetonitril	M
Acid lactic	0,5	Acrilonitril	M
Acid lauric	1	Acetamidă	1
Acid oleic	2	Formamidă	0,5

* M = miscibil

Principii generale privind solubilitatea in CO_2 supercritic

- Puterea de solvatare a CO_2 creste cu P pana la valoarea coresp. CO_2 lichid;
- Cu cresterea puterii de solvatare scade selectivitatea;
- Sunt solubili:
  - Compusii oxigenati si cei lipofili cu M mica si medie (cetone, esteri, alcooli, eteri, aldehide, lactone);
  - Compusii polari cu M mica (acizi carboxilici)

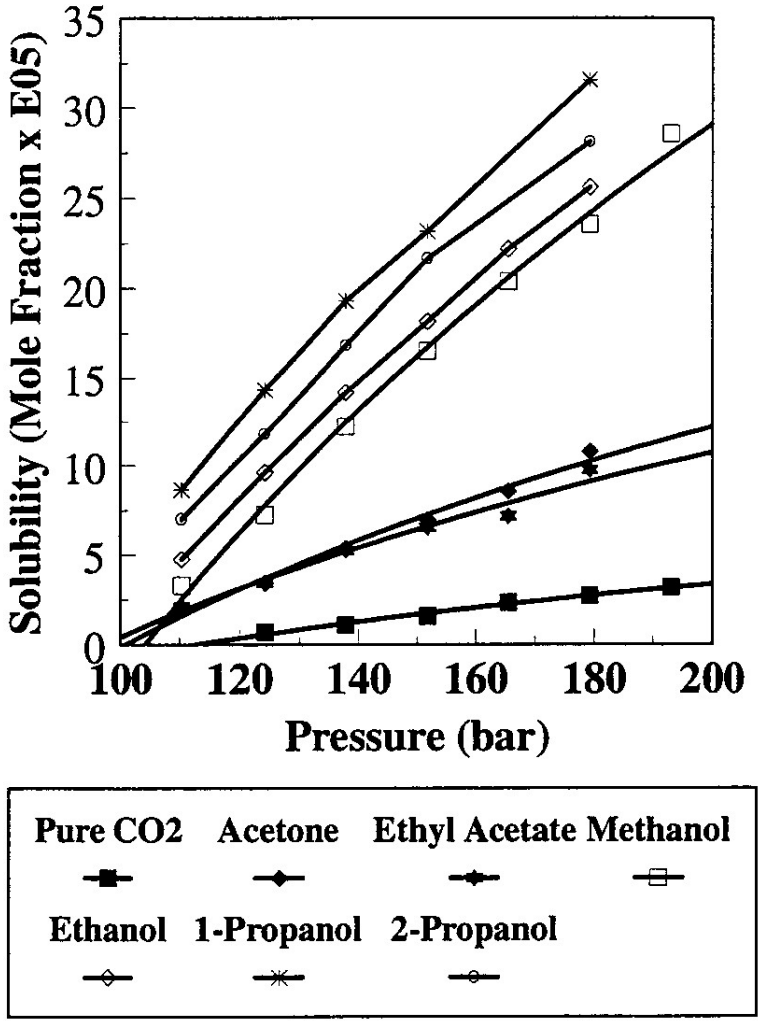
M – masa moleculara

Principii generale privind solubilitatea in CO_2 supercritic

- Intr-o familie de compusi, solubilitatea scade cu cresterea M;
- Gruparile polare (-OH, -COOH, -NO_2) reduc solubilitatea substantelor in FSC;
- Glucidele si aminoacizii nu sunt solubili in CO_2 SC;
- Solubilitatea apei la 20 °C = 0,1%

Principii generale privind solubilitatea in CO_2 supercritic

- Adaugarea unei mici cantitati de compus polar (metanol, apa, etc.) in CO_2 SC, duce la solubilizarea compusilor polari;
- Sol. Naproxen in CO_2 SC la 333,1 K, cu adaus de 3,5% mol cosolvent [Ting et al., 1993]



Solubility Studies of Co-solvent Modified SF-CO_2
Ind. Eng. Chem. Res., 26, 56 (1987)

1. Dynamic Solubility Apparatus
2. Gravimetric Method
3. Reproducibility ≈5%
4. 3.5% Modifier (mole)

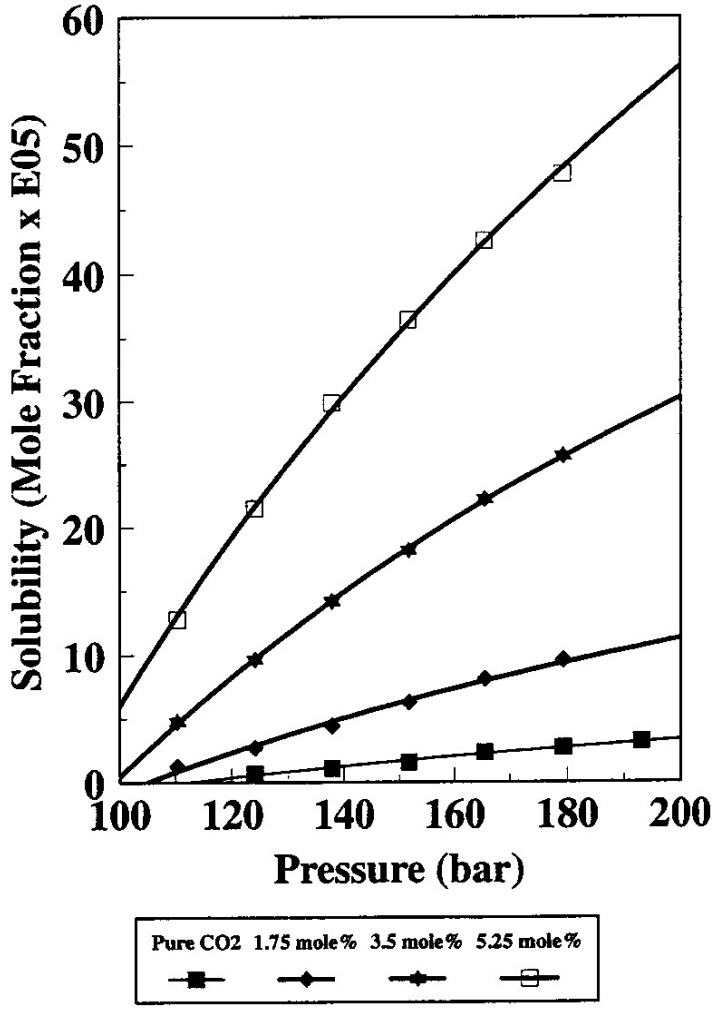
Cosolvent- Induced Solubility Enhancements of Solids in Carbon Dioxide at 35°C and at a density of 20.5 g-mol/L

Solid	Cosolvent	Solubility Enhancement
Benzoic acid	Methanol	3.7
	Acetone	2.1
	N-octane	2.3
2-aminobenzoic acid	Methanol	7.2
	Acetone	3.1
Phthalic anhydride	Acetone	1.7
Hexamethylbenzene	Methanol	1.1
	Acetone	1.2
	N-octane	2.1
	N-pentane	1.8
Acridine	Methanol	2.3
	Acetone	1.7
2-naphthol	methanol	4.5

High melting solids chosen that have low solubility in SF-CO_2
See also Ind. Eng. Chem., 26, 1476 (1987)
Modifiers may also be surfactants, water, complexing agents.

Principii generale privind solubilitatea in CO_2 supercritic

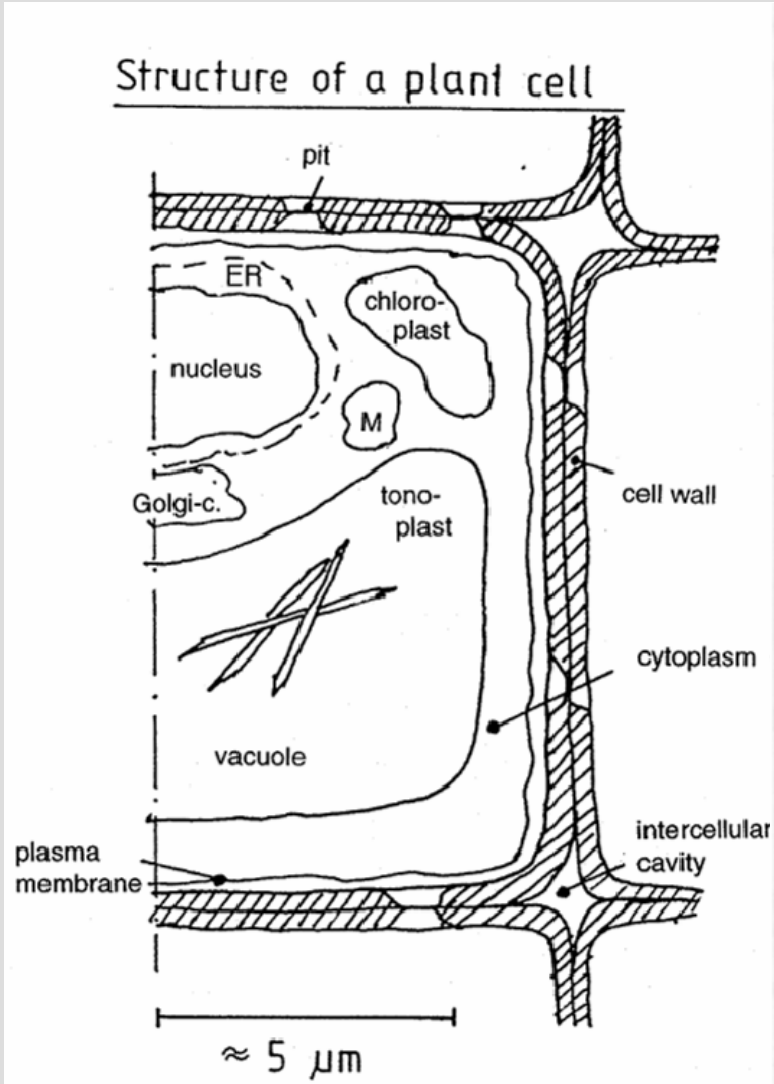
- Solubilitatea creste cu cresterea continutului de cosolvent polar:
- Sol. Naproxen in CO_2 SC la 333,1 K, cu adaus variabil de etanol in calitate de cosolvent [Ting et al., 1993]

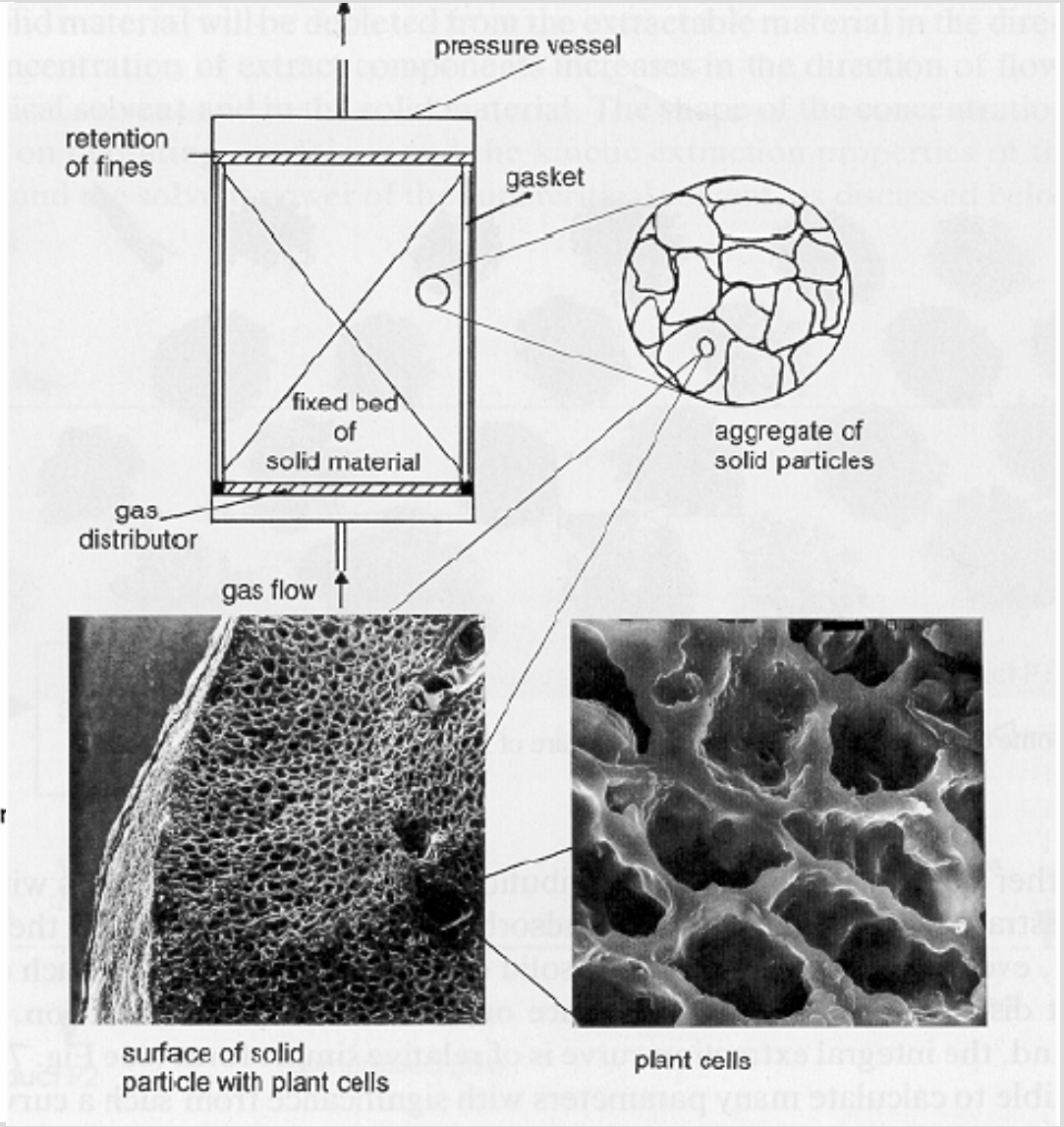


Principii generale privind solubilitatea in CO_2 supercritic

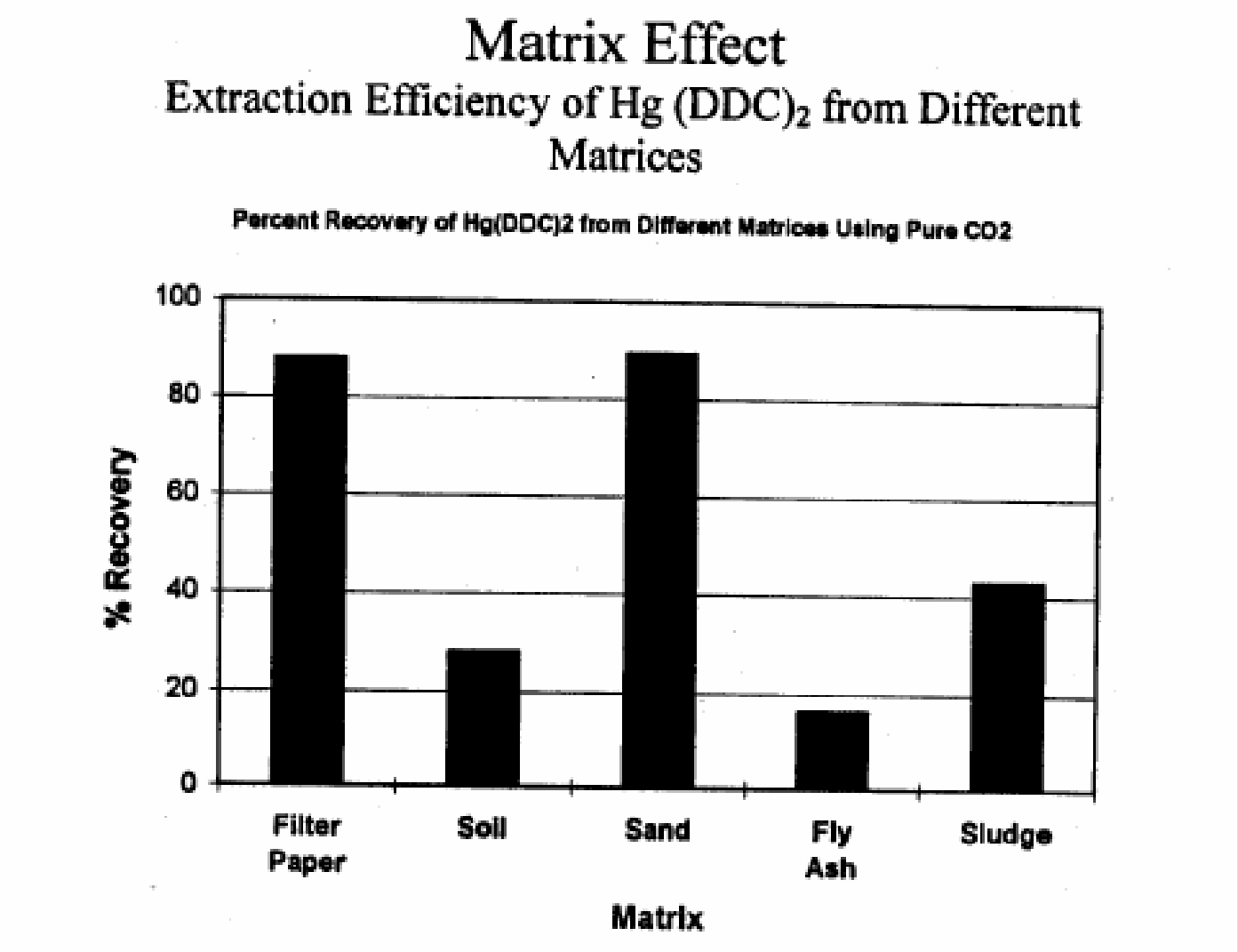
- Solubilitatea in FSC nu implica in mod automat EXTRACTIBILITATEA din matrice.
- EX:
  - Cafeina este solubila in CO_2 SC, dar acesta nu poate extrage cafeina din boabe de cafea uscate.
  - Este necesara umezirea boabelor (modificarea matricii).

Exemplu de matrice vegetala





Principii generale privind solubilitatea in CO_2 supercritic



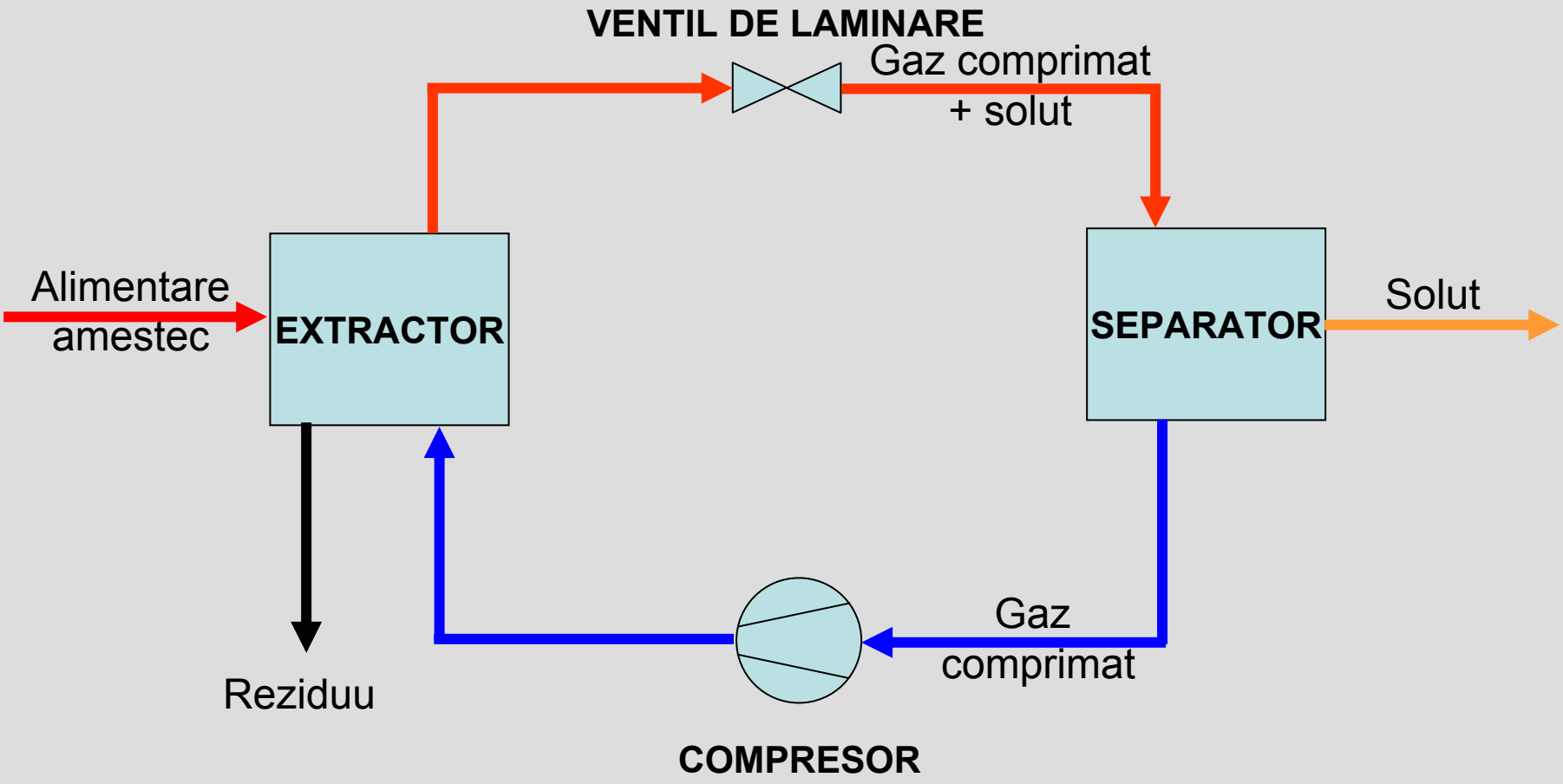
Solubilitatea in CO_2 lichid si supercritic

Clasificarea unor compuşi naturali în funcţie de solubilitatea în dioxidul de carbon lichid şi supercritic (Moyler, 1989).

Foarte solubili	Cu solubilitate medie	Virtual insolubili
- hidrocarburi alifatice uşoare - esteri - eteri - cetone - alcooli - acizi carboxilici - compuşi organici cu M<250	- hidrocarburi alifatice grele - derivaţi ai terpenelor - esteri - carotenoizi - compuşi polari cu grupări $-NH_2$ şi -SH - lipide saturate şi nesaturate - compuşi organici cu M<400	- glucide - proteine - polifenoli - ceruri - săruri anorganice - aldehide cu M mare - compuşi organici cu M>400

Procedee de extractie supercritica

- Extractie cu contact unic

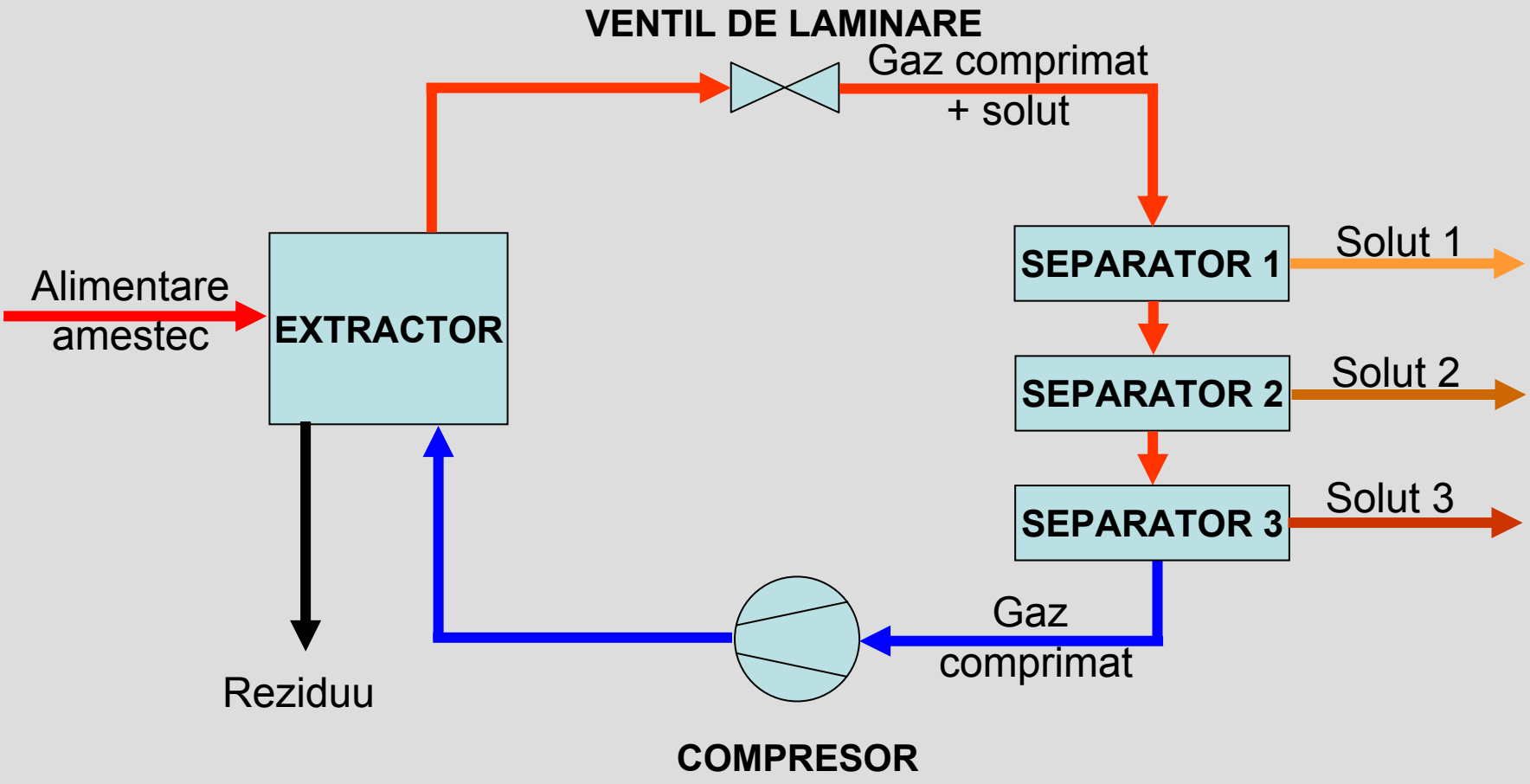


Extractia cu contact unic

- unul sau mai multi componenti din amestec se solubilizeaza selectiv in fluidul SC;
- timpul de solubilizare este variabil;
- sistemul este separat (modificand P si T);
- fluidul SC este comprimat si recirculat

Procedee de extractie supercritica

- Extractie multipla

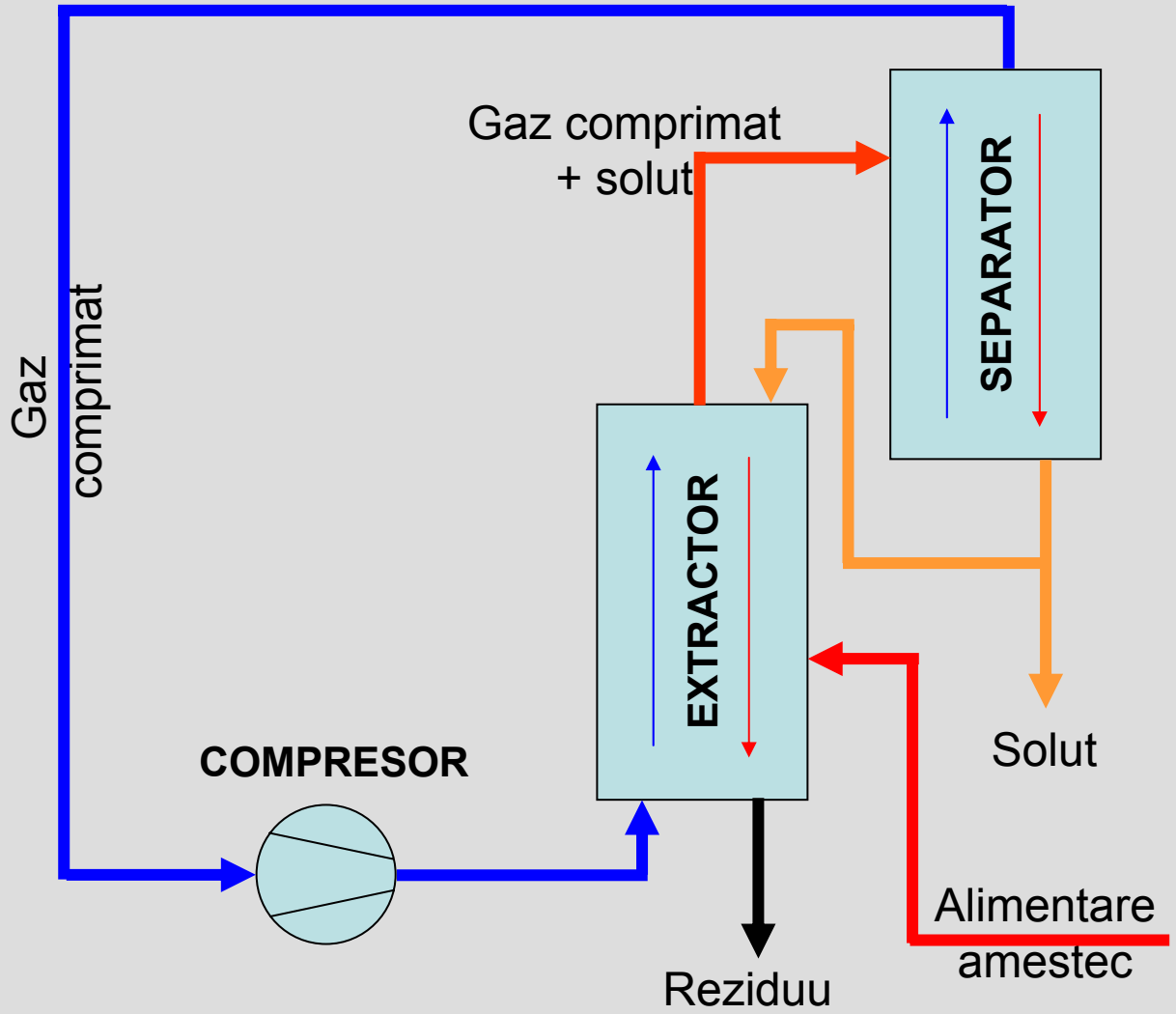


Extractia multipla

- se aplica atunci cand factorul de separare are valori scazute (selectivitate mica de separare)
- separarea componentilor extrasi:
  - modificarea in trepte a cond. de extractie
  - modificarea in trepte a cond. de separare

Procedee de extractie supercritica

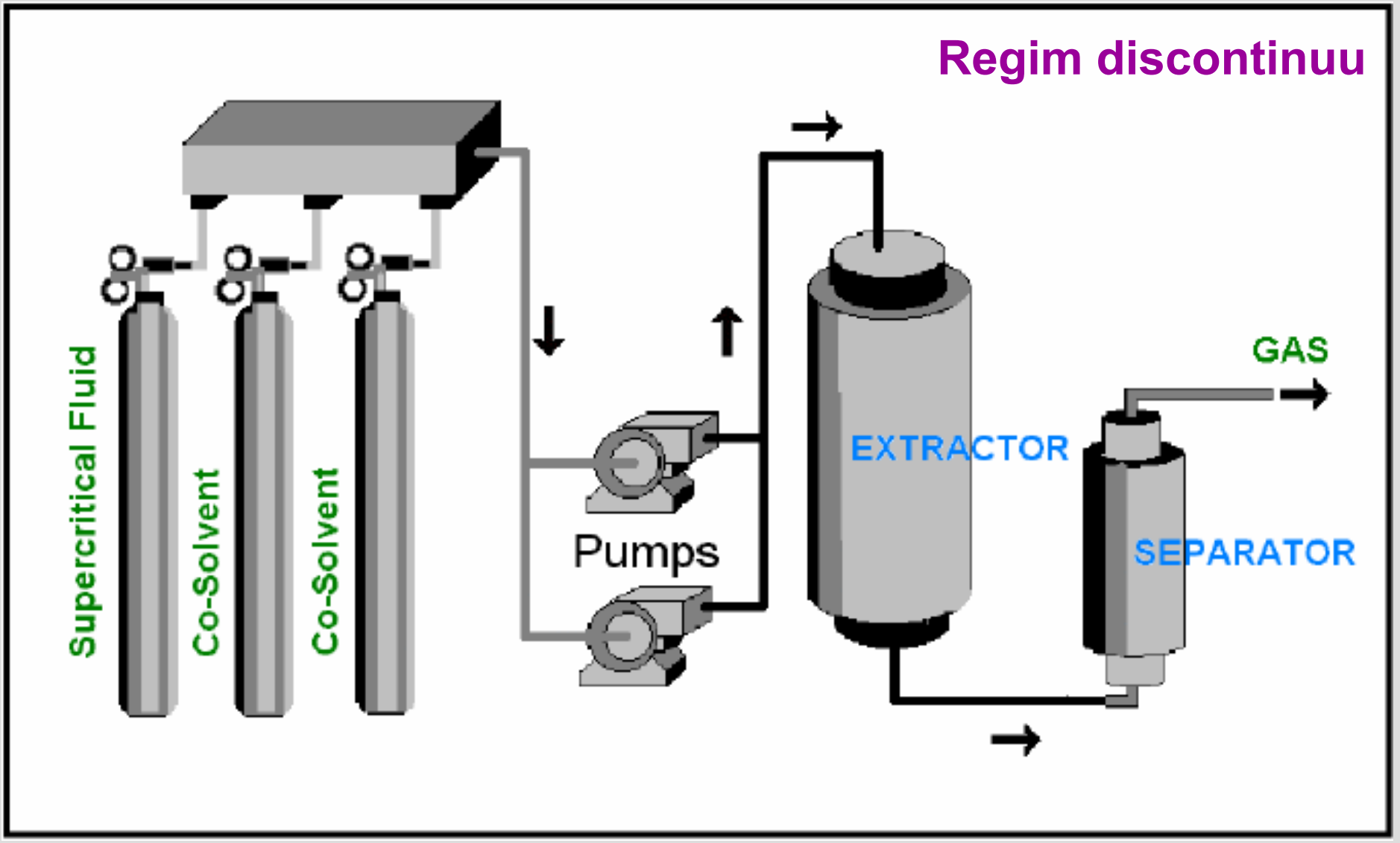
- Extractie multipla in contracurent



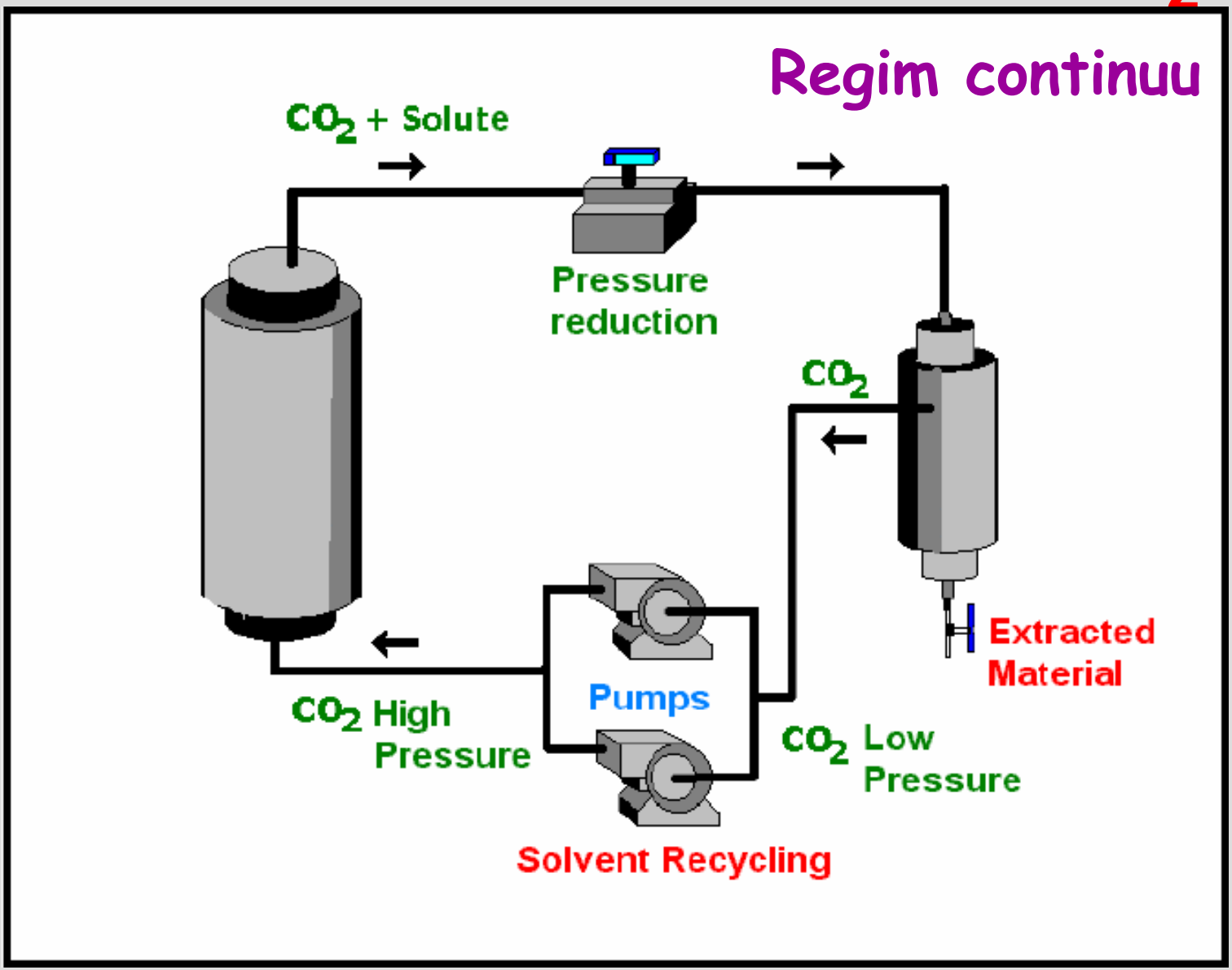
Extractia multipla in contracurent

- Proces similar extractiei L - L

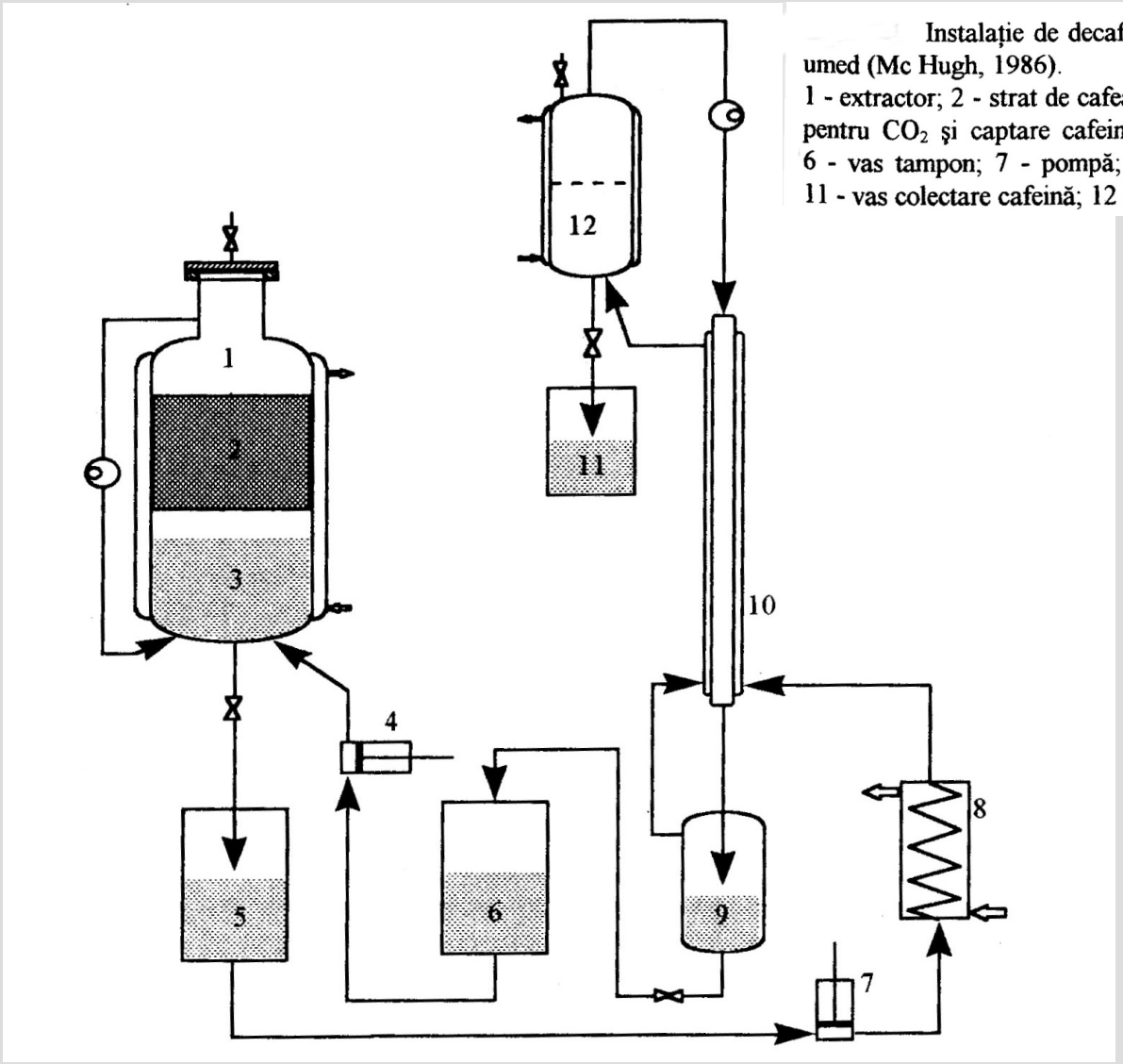
Instalatii de extractie cu CO_2 SC



Instalatii de extractie cu CO_2 SC

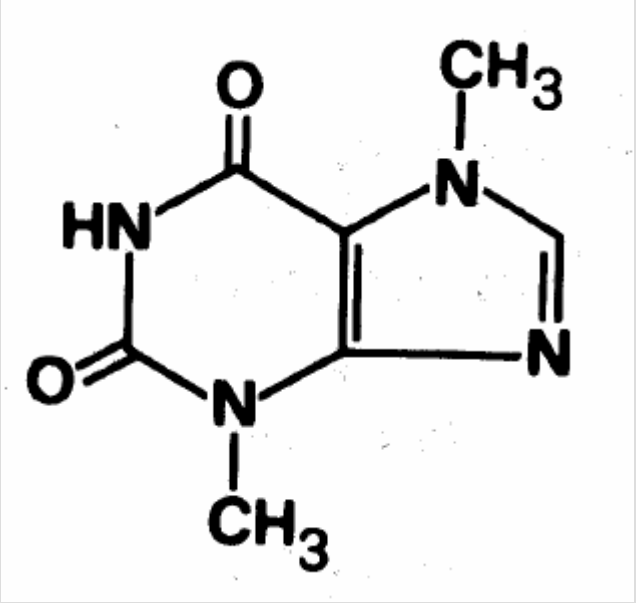


Decafeinarea boabelor de cafea

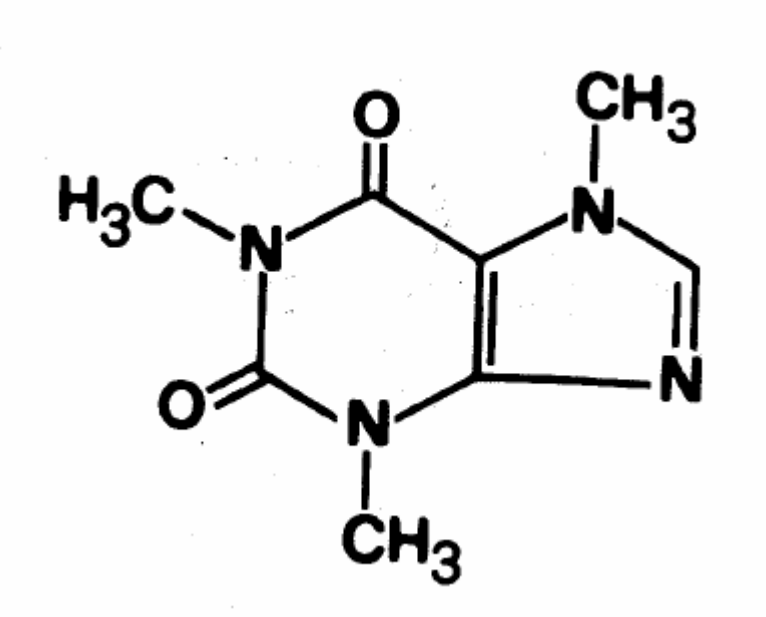


Instalație de decafeinizare din boabe de cafea verde cu CO_2 supercritic umed (Mc Hugh, 1986).
1 - extractor; 2 - strat de cafea verde boabe umezită; 3 - secțiune de umezire cu apă pentru CO_2 și captare cafeină; 4 - compresor; 5 - vas colectare soluție cafeină; 6 - vas tampon; 7 - pompă; 8, 10 - schimbătoare de căldură; 9 - vas separare; 11 - vas colectare cafeină; 12 - vas concentrare soluție cafeină.

Decafeinarea boabelor de cafea

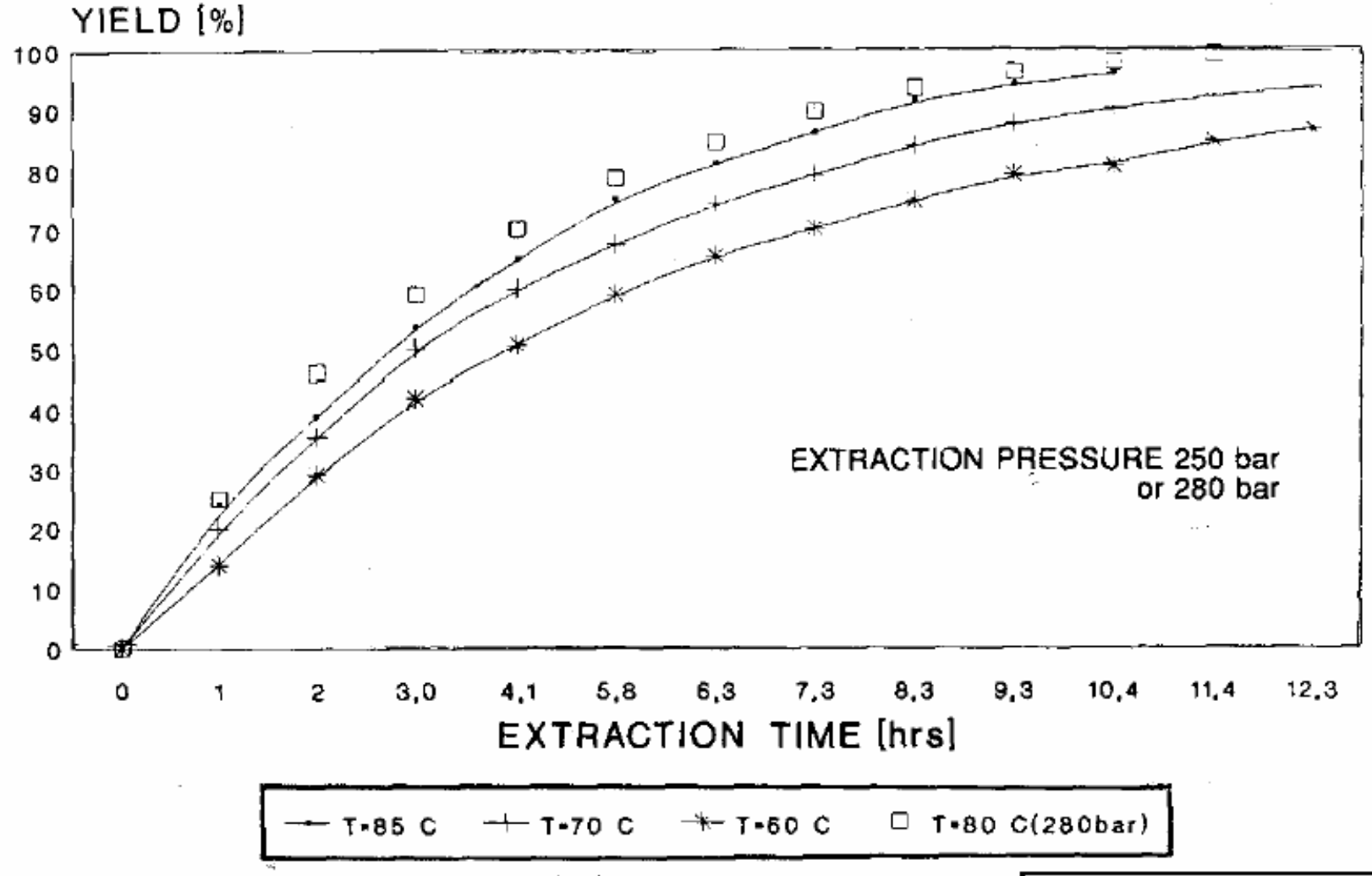


THEOBROMINA



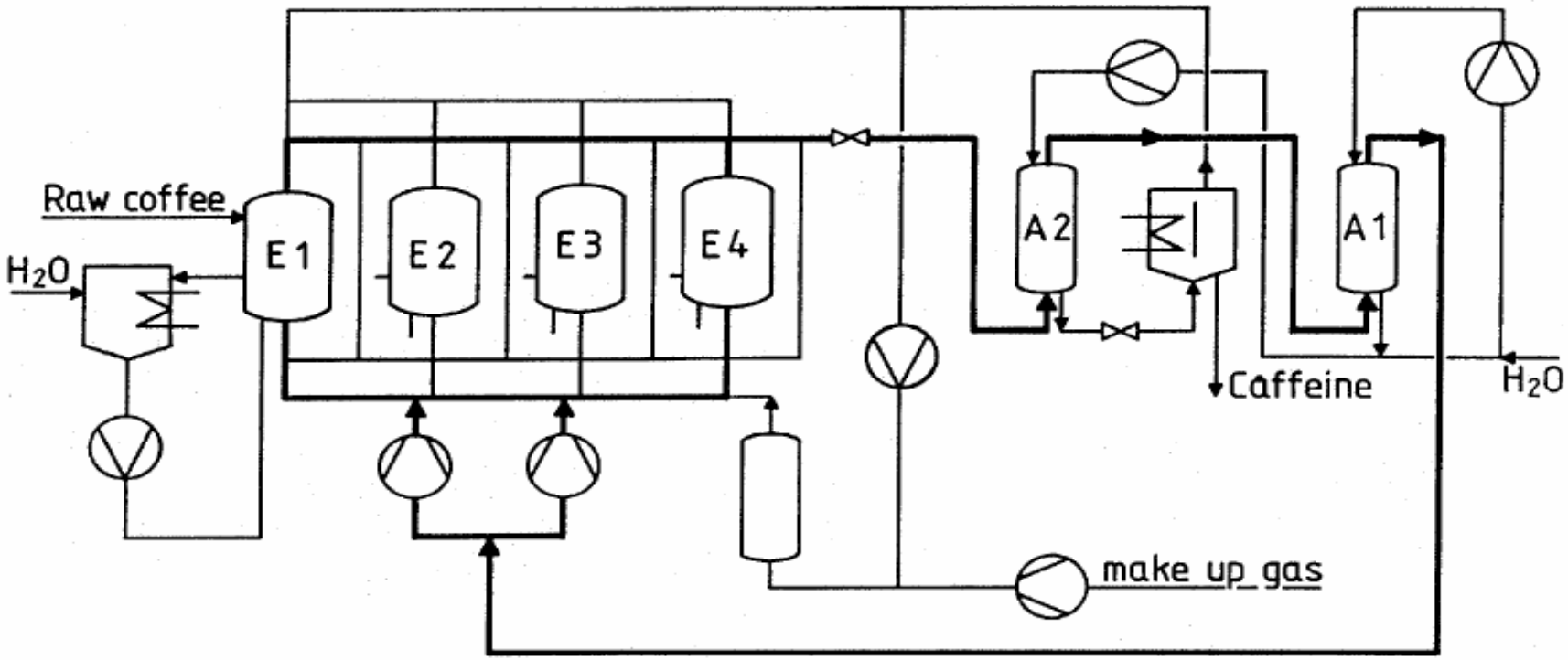
CAFEINA

Decafeinarea boabelor de cafea



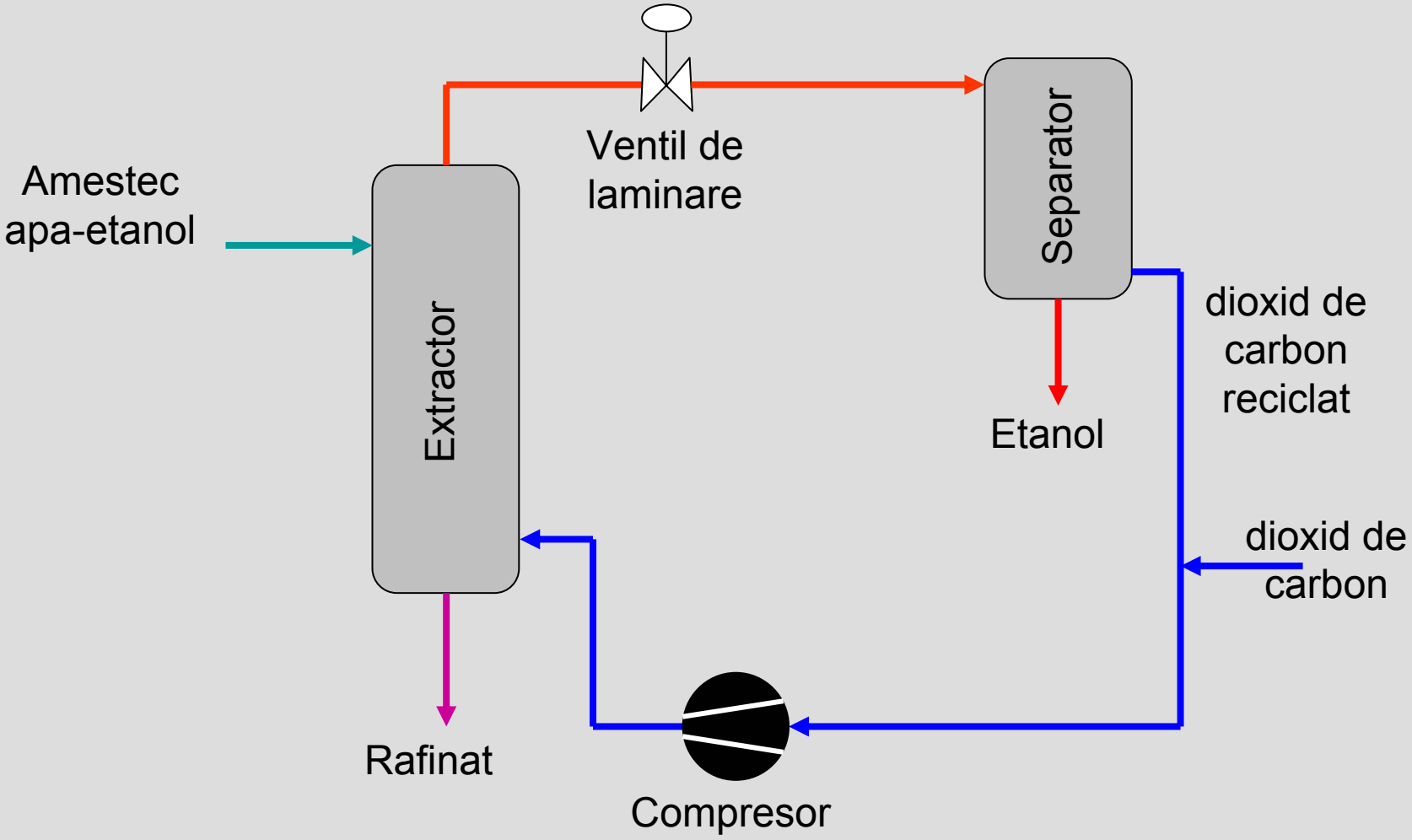
Lack and Seidlitz 1993

Instalatie de extractie a cafeinei in mai multe trepte

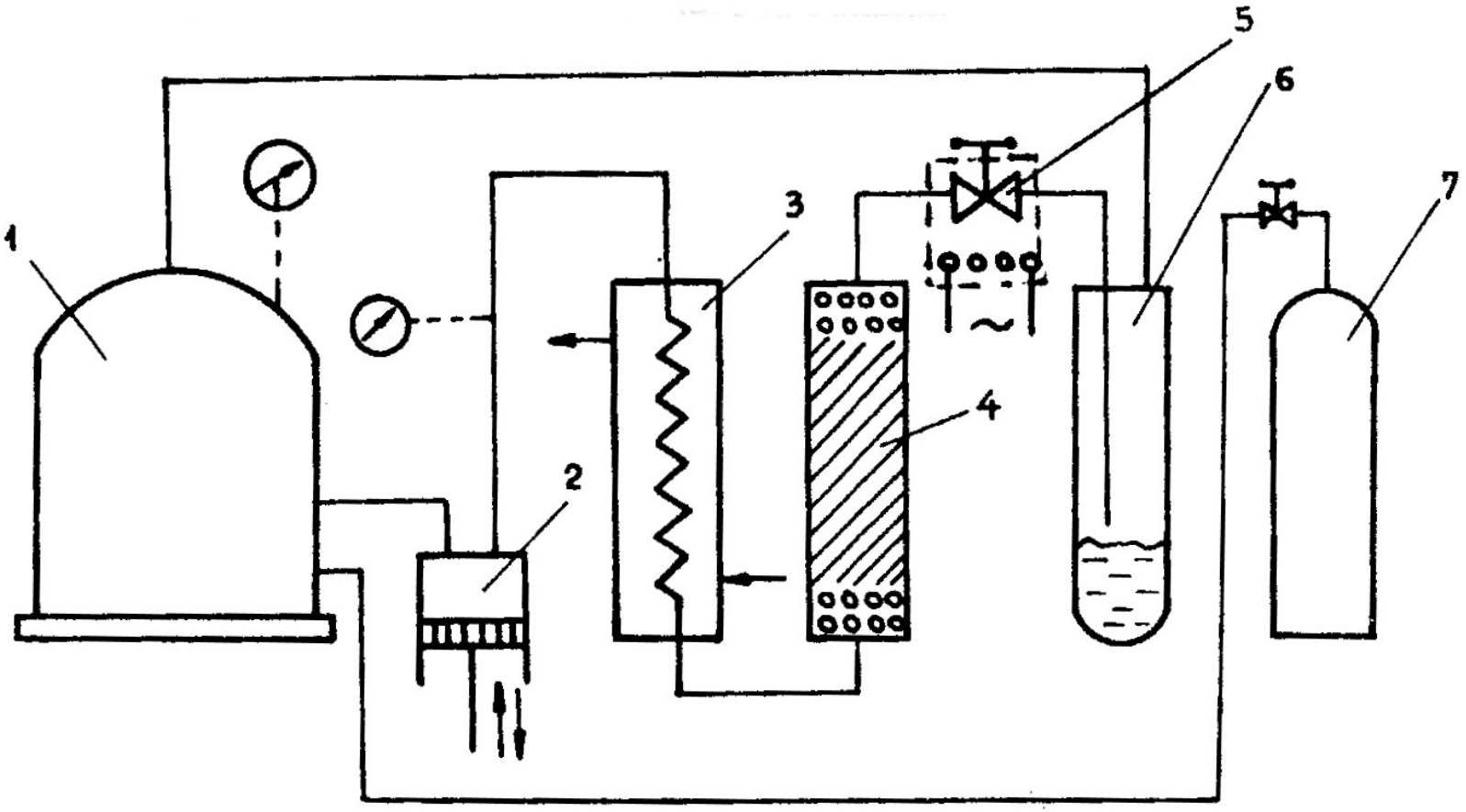


E - Extractor
A - Separator

Imbogatirea etanolului (eliminarea apei) cu CO_2 SC



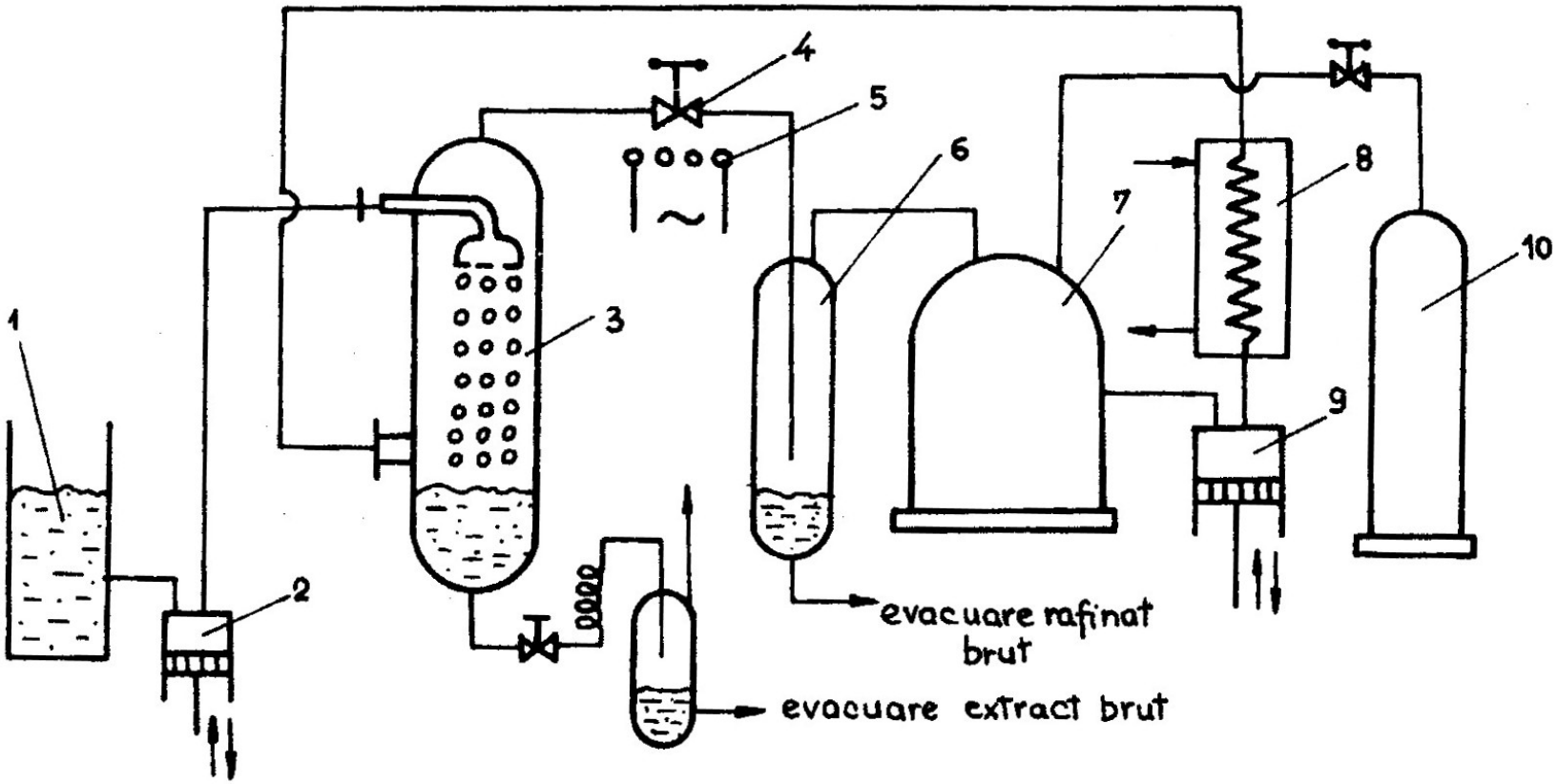
Instalatii de extractie cu CO_2 SC



Instalație de spălare extractivă cu fluid supercritic în circuit închis

1- vas tampon; 2- compresor; 3- condensator; 4- extractor; 5- ventil detentă; 6- tub colector; 7- butelie de gaz

Instalatii de extractie cu CO_2 SC



Instalație de extracție lichid - lichid cu solvent supercritic

1- rezervor amestec inițial; 2- pompă de presiune mare; 3- extractor; 4- ventil detentă; 5- încălzitor; 6- tub colector; 7- rezervor de gaz; 8- condenstor; 9- compresor; 10- butelie gaz

Aplicatii industriale

Table 1: Industrial Applications[28]

Year	Operating company	Processed material
1982	SKW/Trotsberg	Hops (Hamei)
1984	Fuji Flavor Co.	Tobacco
	Barth and Co.	Hops
	Natural Care Byproducts	Hops, Red Pepper
1986	SKW/Trotsberg	Hops
	Fuji Flavor Co.	Tobacco
	CEA	Aromas, Pharmaceuticals
1987	Barth and Co.	Hops
	Messer Griesheim	Various
1988	Nippon	Tobacco
	Takeda	Acetone residue from antibiotics
	CAL-Pfizer	Aromas
1989	Clean Harbors	Waste waters
	Ensco, Inc	Solid wastes
1990	Jacobs Suchard	Coffee
	Raps and Co.	Spices
	Pitt-Des Moines	Hops
1991	Texaco	Refinery wastes
1993	Agisana	Pharmaceuticals from botanicals
	Bioland	Bones
1994	AT&T	fiber optics rods

Aplicatii industriale

Firm	Application	Throughput	Date of Start-up
SKW Trotsberg AG (Trotsberg, Germany)	tea decaffeination	6,000 t/y	1988
Kraft General Food (Houston, US)	coffee decaffeination	200,000 t/y	1988
Philip Morris Cos. Inc. (Chester, US)	removal of nicotine from tobacco		
US Hop Extraction Crop (Yakima, US)	hop extraction	4,400-8,800 t/y	1990
Camilli Albert & Laloue (Grass, US)	extraction of flavour essences from plants		1989
Flavex GmbH (Rehlingen, Germany)	extraction of aroma and cosmetic components from plant material	220 - 3,650 t/y	

Aplicatii industriale

Year	Operating company	Processed material
1982	SKW/Trotsberg	Hops
1984	Fuji Flavor Co. Barth and Co. Natural Care Byproducts	Tobacco Hops Hops, Red Pepper
1986	SKW/Trotsberg Fuji Flavor Co. CEA	Hops Tobacco Aromas, Pharmaceuticals
1987	Barth and Co. Messer Griesheim	Hops Various
1988	Nippon Takeda CAL-Pfizer	Tobacco Acetone residue from antibiotics Aromas
1989	Clean Harbors Ensco, Inc	Waste waters Solid wastes
1990	Jacobs Suchard Raps and Co. Pitt-Des Moines	Coffee Spices Hops
1991	Texaco	Refinery wastes
1993	Agisana Bioland	Pharmaceuticals from botanicals Bones
1994	AT&T	fiber optics rods

The Use of Supercritical Fluid Extraction Technology in Food Processing
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Featured Article - Food Technology Magazine, June 2002
The World Markets Research Centre, London, UK

Instalatie de extractie cu CO_2 SC
Capacitate: 2 x 400 L

Indepartarea colesterolului din produse de origine animala

Table 2: Supercritical Fluid Extraction of Cholesterol with CO_2 from Products of Animal Origin

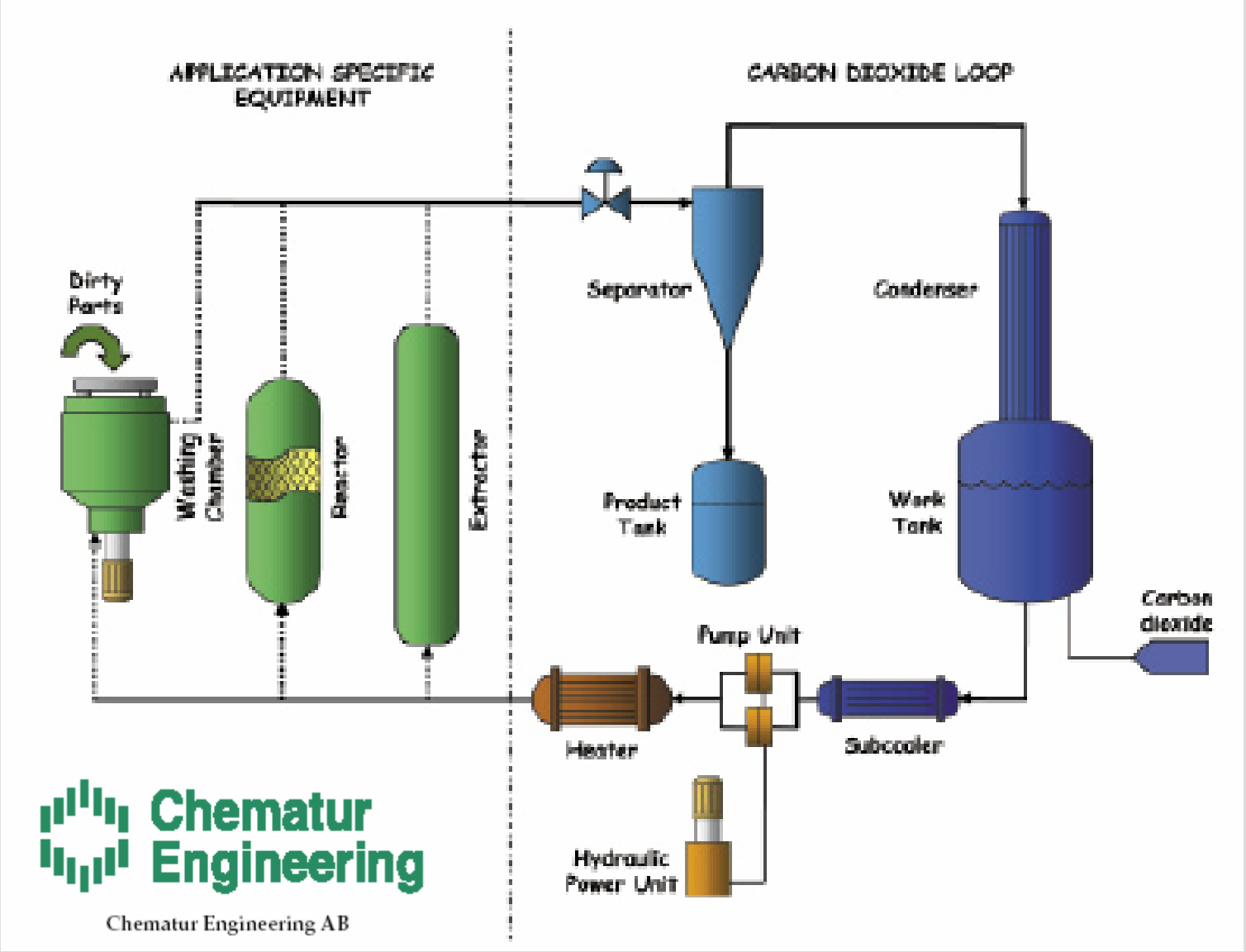
Product	Reference	P(MPa)	T(°C)	Cholesterol(mg/g)		Yield(%)
				Before	After	
Dried egg yolk	(Froning, et al., 1990)	16.5-37.8	40-55	18.52	6.34	65.8
Dried egg yolk	(Bohac, 1998)	24.1-37.8	45-55	18.94	0.38	98.0
Dehydrated beef	(Lim, 1992)	23.4-38.6	45-55	1.56	0.19	87.8
Beef patties (cooked)	(Fenton and Sim, 1992)	17.2-55.1	40-50	1.94	0.12	93.8
Pork (cooked)	(Lin, et al., 1999)	7.3-34.4	50-150	0.80	0.22	70.1
Dried chicken meat	(Froning, et al. 1994)	30.6-37.6	45-55	4.96	0.54	90.0
Milk fat	(Mohamed, et.al., 1998)	10.1-36.4	40-70	2.50	0.21	91.5
Milk fat*	(Mohamed, et al., 2000)	8.0 -24.0	40-70	2.50	0.20	93.4

*Using supercritical ethane as solvent

Instalatii industriale de extractie cu FSC

Flowrate	40 to 20 000 kg/h
Pressure	500 bar
Temperature	100 to 200 °C

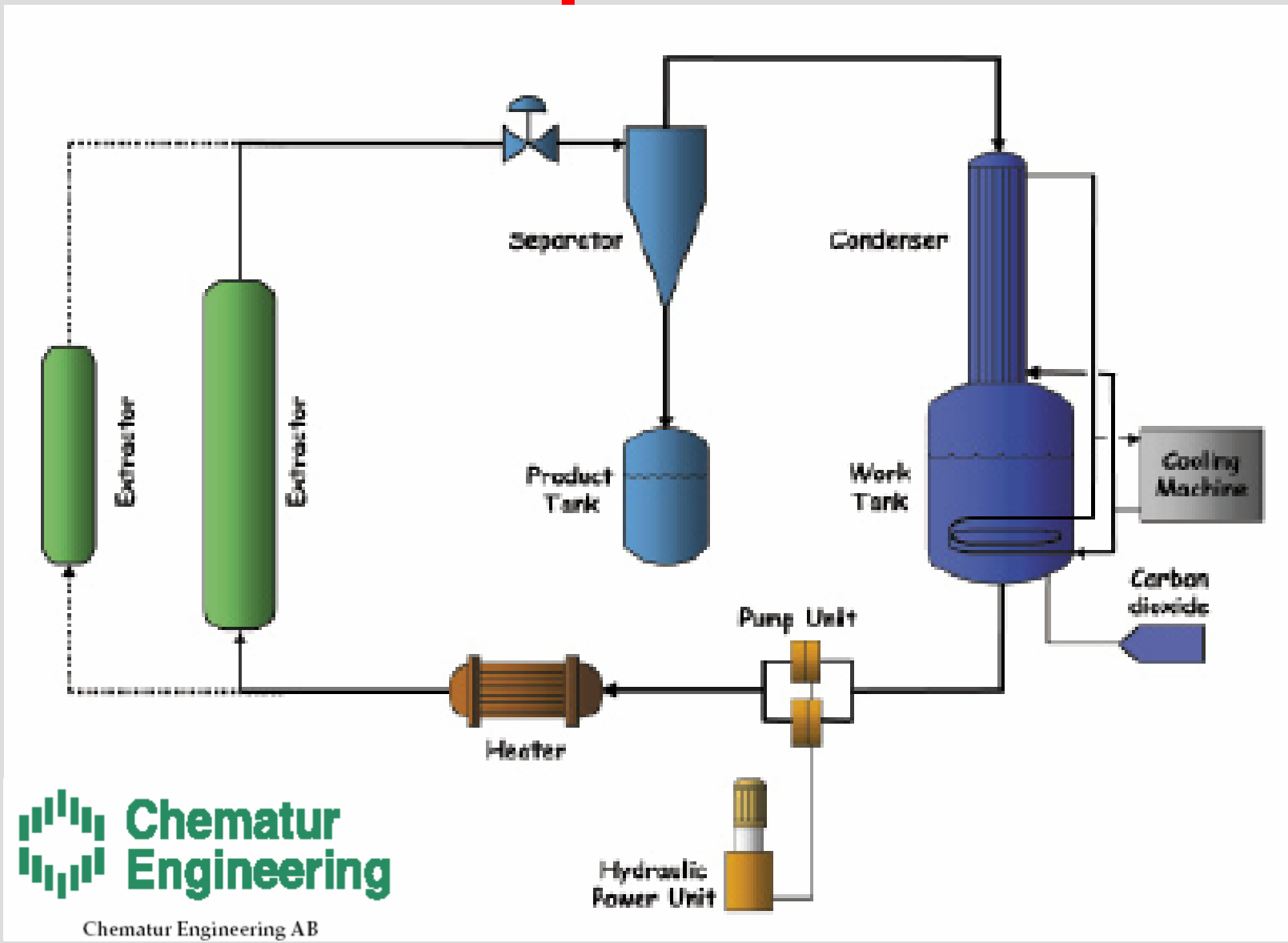
Instalatii industriale de extractie cu FSC



Extractorul pilot XTractor™

Extractor volume	2 and 10 L
Max CO_2 flow	50 L/h
Max pressure	500 bar
Max temperature	100 °C
Separation	~ 55 bar
Optional 1st separation	max 200 bar

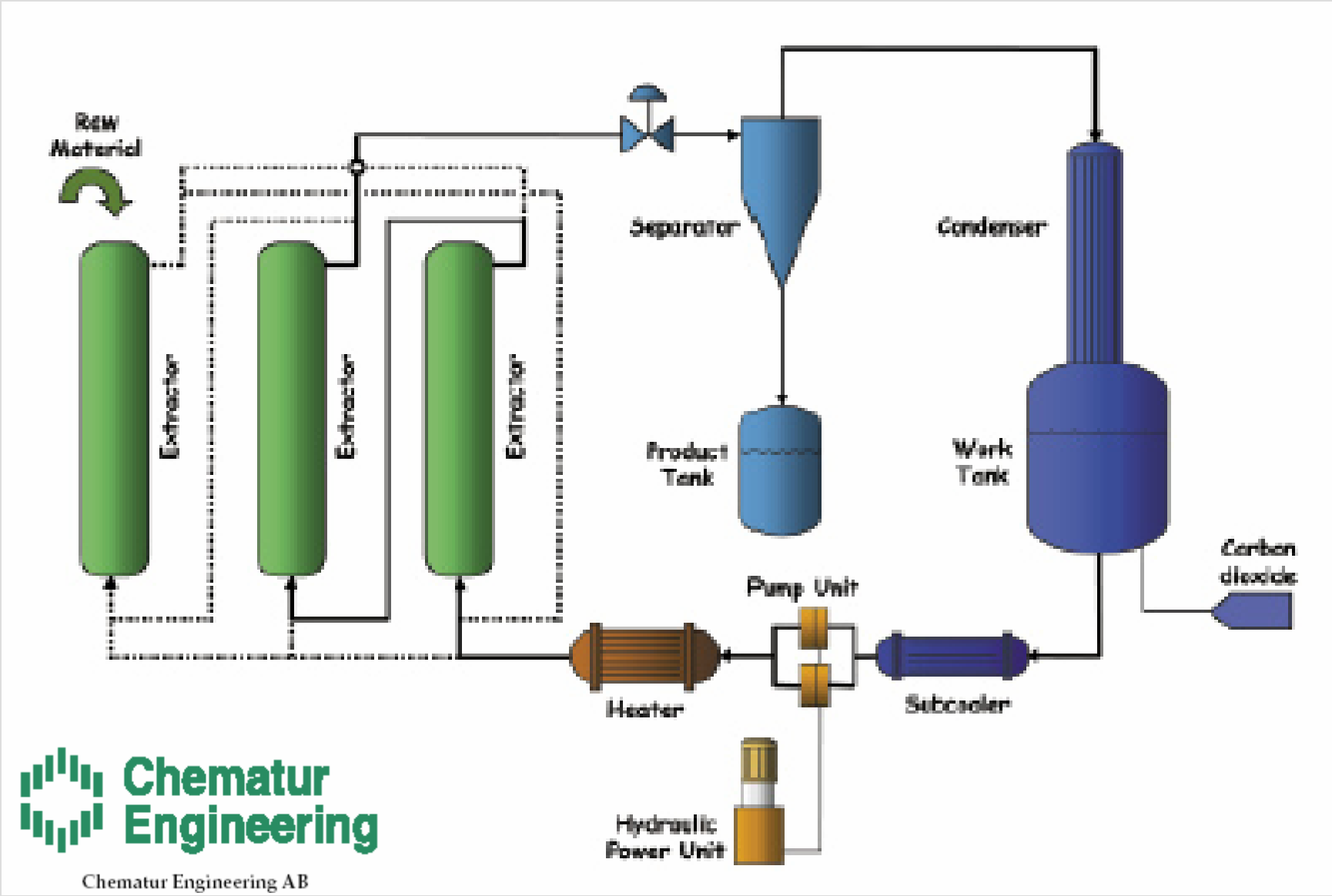
Extractorul pilot XTractor™



Extractorul industrial XTractor™

Extractor volume	3 x 200 L
Max pressure	500 bar
Max CO_2 flow	1 000 L/hour
Max temperature	100 °C
Separation	50 - 80 bar
Optional 1st separation	max 200 bar

Extractorul industrial XTractor™



Extractie cu fluide supercritice

Herbs and Spices: IERBURI SI CONDIMENTE

Arnica		Garlic	Usturoi	Scortisoara	Cinnamon
Eucalyptus	Eucalipt	Rosemary	Rozmarin	Nucsoara	Nutmeg
Parsley	Patrunjel	Caraway seed			Tumeric
Anis seed	Seminte de anason	Ginger	Ghimbir	Cuisoare	Clove
Evening primrose	Primula de seara	Rosehip		Ceapa	Onion
Peppermint leaves	Frunze de menta	Cardamom		Cimbru	Tyme
Basil	Busuioc	Ginseng		Coriandru	Coriander
Fennel		Sage oil	Ulei de salvie		Oregano
Pyrethrum		Celery seed	Seminte de telina	Vanilie	Vanilla bean
Black currant seed	Seminte de stafide	Kava root	Radacina de Kava		Cumin
Feverfew		St. John's wort			Paprika
Black pepper	Piper negru	Chili			Dill seed
Camomile	Musetel	Marigold	Galbenele		Neem

Extractie cu fluide supercritice

Specialty Oils: ULEIURI SPECIALE

Grape seed	Seminte de struguri	Black currant seed	Seminte de stafide	Pumpkin seed	Seminte de dovleac
Wheat germ oil	Ulei de germeni de grau	Evening primrose	Primula de seara	Rice bran oil	Ulei de tarate de orez
Borage oil		Sesame oil	Ulei de susan	Oat oil	Ulei de ovaz

Lipids: GRASIMI

De-oiling of crude lecithin	Fractionation of lipid mixtures	Recovery and separation of tocopherol
Algae	Fractionation of phospholipids	Spent bleaching earth

Others: ALTELE

Decaffeinated tea	Ceai decofeinizat	Expansion of tobacco	Expandare tutun	Defatted cocoa	Cacao degresata
Decaffeinated coffee	Cafea decofeinizata	Impregnation	Impregnare	Coatings	Acoperiri
Hops	Hamei	Bark	Coaja	Fruits	Fructe

Prelucrarea hameiului

- Compozitia tipica a hameiului uscat:

Celuloza & lignina	40%
Rasini (α & β acizi)	15%
Proteine	15%
Apa	10%
Cenusa	8%
Taninuri	4%
Grasimi & ceruri	3%
Pectine	2%
Monozaharide	2%
Uleiuri esentiale	1%

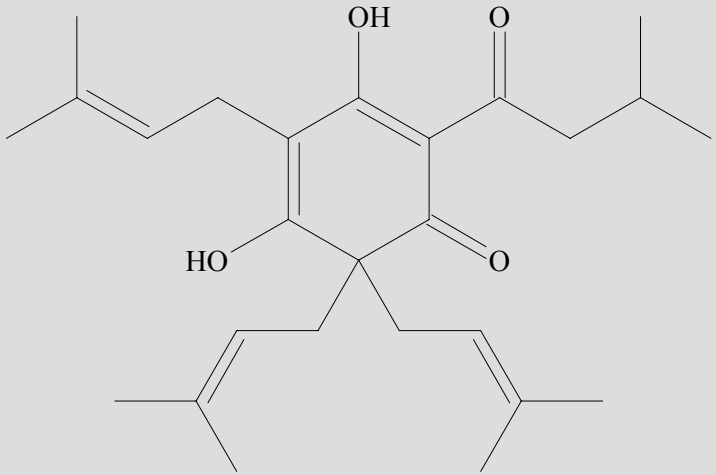
Solventi de extractie - HAMEI

1908	Etanol	Anglia
1942	Diclorometan	Germania
1960	Tricloroetan	Germania
1961	Benzen	Anglia
1965	Metanol	Anglia
1970	Hexan	USA
1980	CO_2 Lichid	Australia/UK
1982	CO_2 Supercritic	Germania

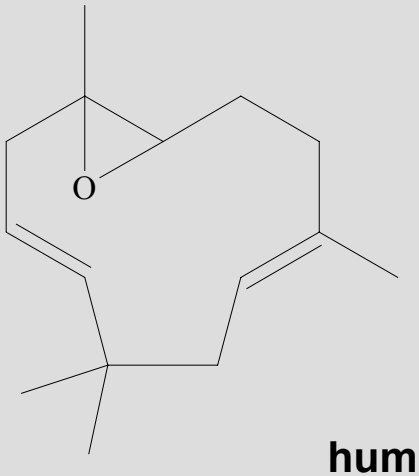
Produse obtinute din hamei

formule anti-microbiene

molecule de arome si parfumuri



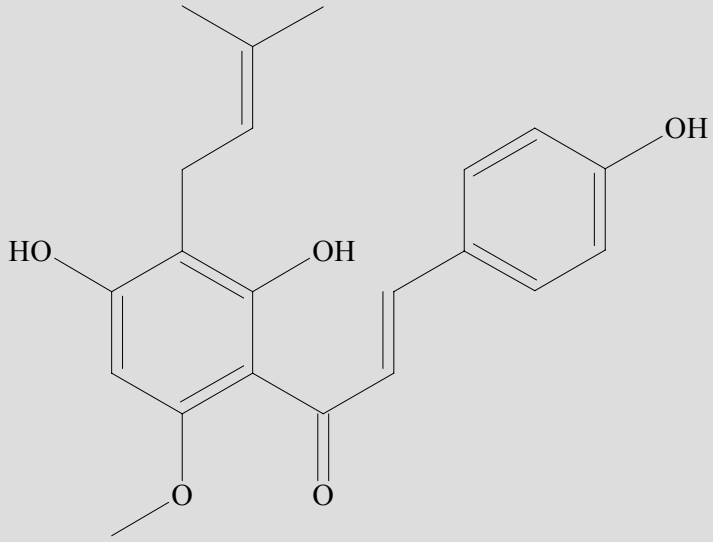
lupulone



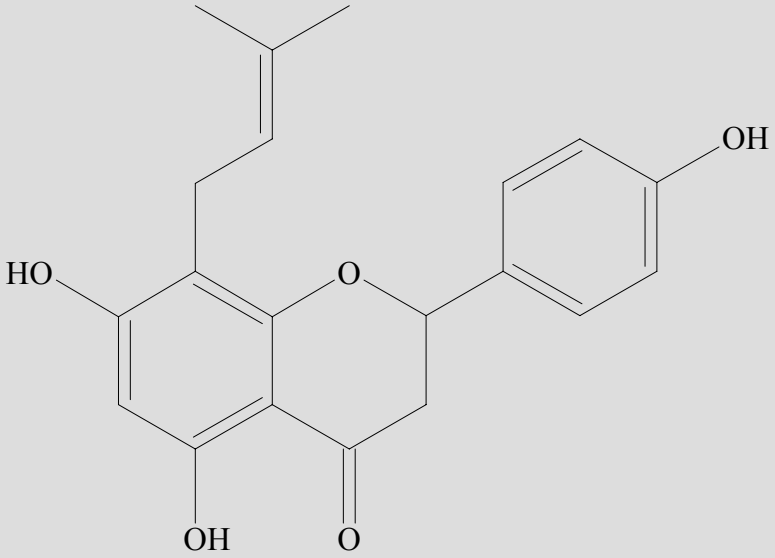
humulene epoxide

Produse obtinute din hamei

Polifenoli

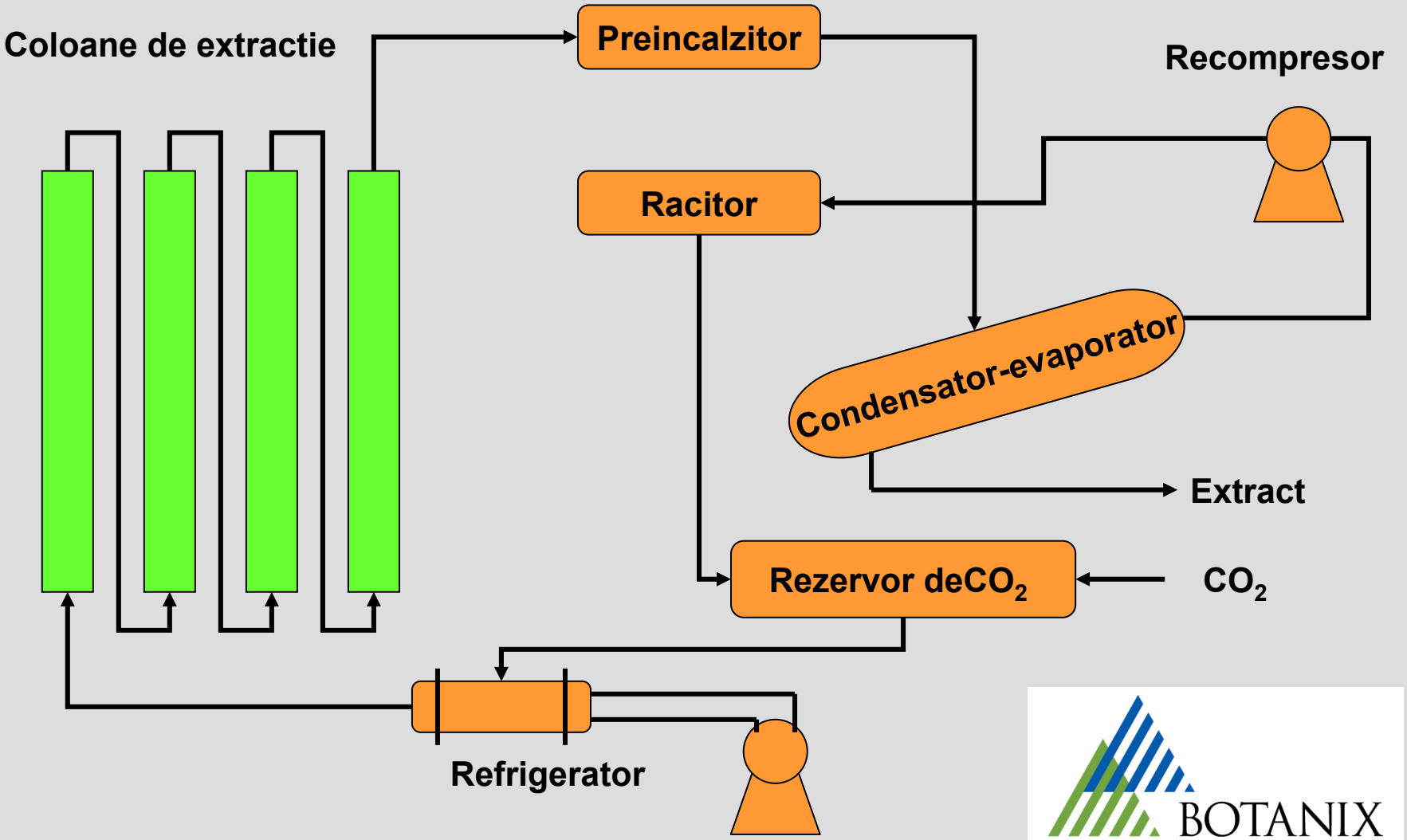


Xanthohumol



8-prenyl naringenin

Extractie cu CO_2 lichid - HAMEI

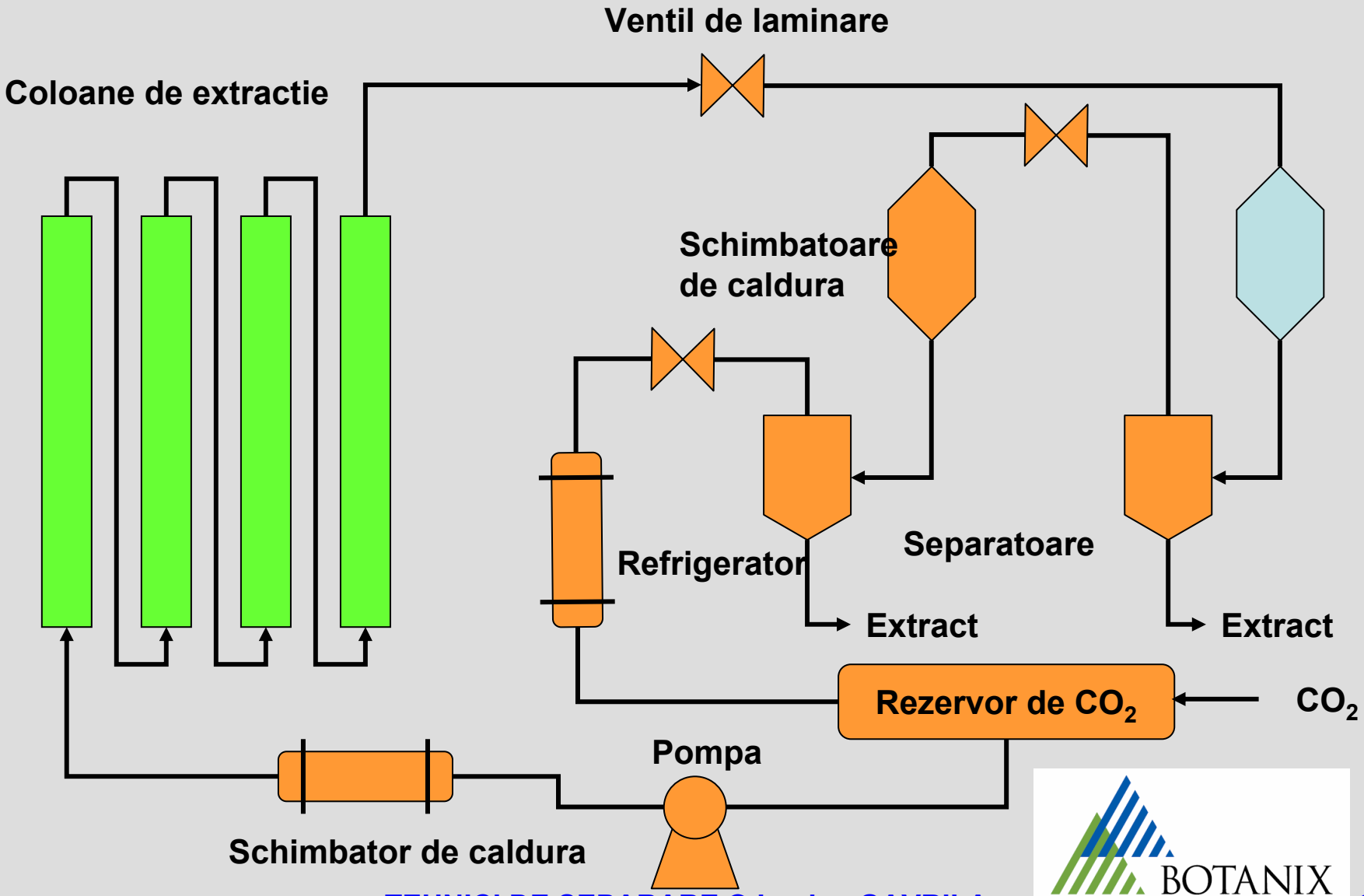


Selectivitatea CO_2 lichid

Lichid	diclorometan	etanol	CO_2 lichid
Alfa acizi	35-45%	30-40%	40-50%
Beta acizi	15-20%	10-15%	18-40%
Alte rasini moi	3-8%	3-8%	5-20%
Rasini tari	2-5%	2-10%	Lipsa
Uleiuri volatile	1-3%	1-2%	2-8%
Grasimi si ceruri	1-2%	Urme	0-5%
Taninuri	Urme	1-5%	Lipsa
Clorofila	<1%	Urme	Lipsa
Saruri anorganice	<1%	0.5-1%	Urme
Solvent rezidual	<1%	0.01-0.1%	Lipsa
Apa	Urme	1-5%	1-5%
Randament tipic	28%	38%	19%

BOTANIX

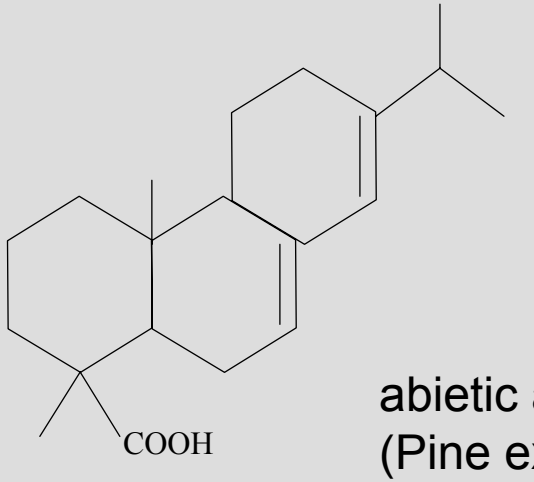
Extractie cu CO_2 supercritic - HAMEI



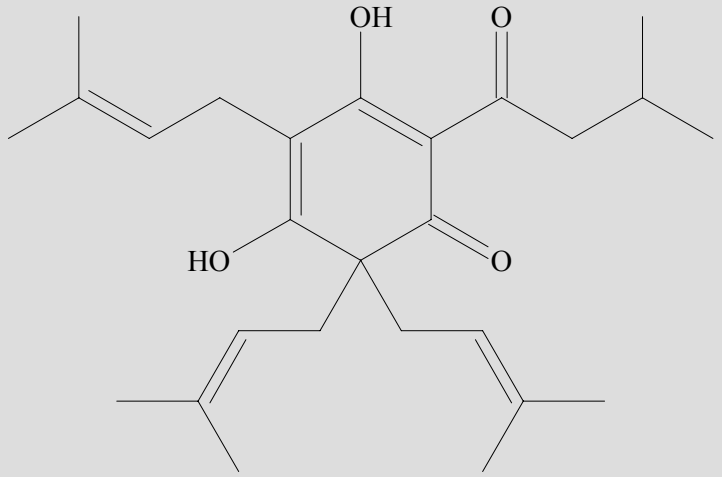
BOTANIX

Extracte din plante

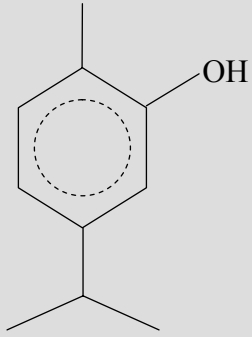
Extracte si molecule antimicrobiene



abietic acid
(Pine extract)



co-lupulone
(Hop extract)



carvacrol
(Origanum extract)

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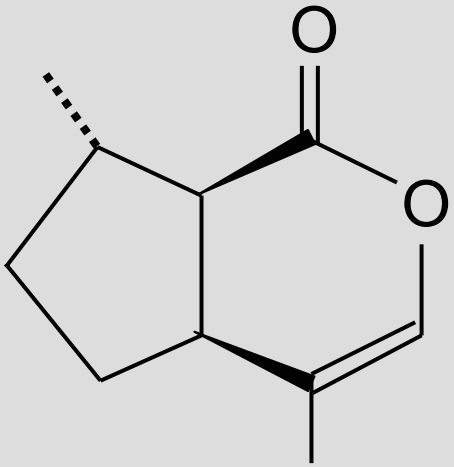
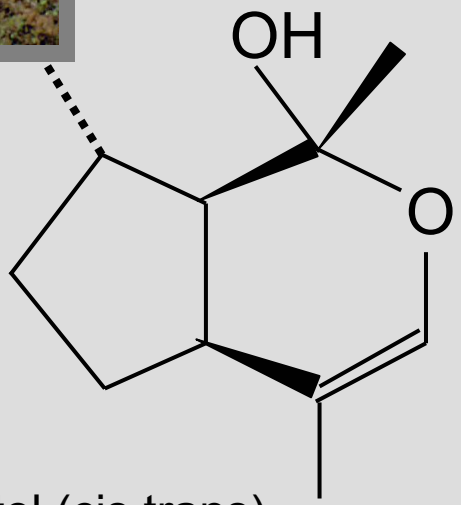
Extracte si molecule antimicrobiene

- Cele mai multe sunt terpenoide din plante aromatice
- Utilizate curent in:
  - extractia zaharului din sfecla si trestie - inlocuiesc formaldehida si sulfitii
  - producerea berii - inlocuiesc Nisinul
  - conservarea alimentelor - inlocuiesc hidroxibenzoatii
  - produse de igiena orala - inlocuiesc triclosanul
  - furaje - inlocuiesc antibioticele
  - biofouling

Antidaunatori naturali



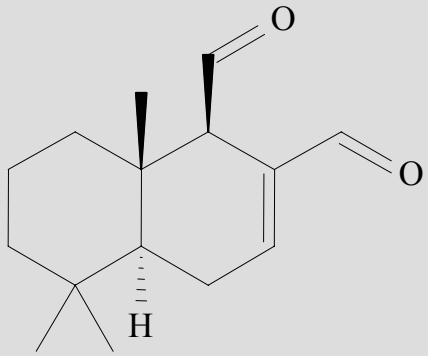
(4aS,7S,7aR)-nepetalactone (cis,trans)



(4aS,7S,7aR)-nepetalactol (cis,trans)

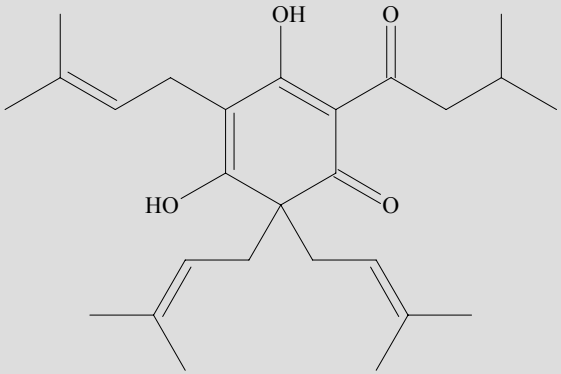
BOTANIX

Antidaunatori naturali



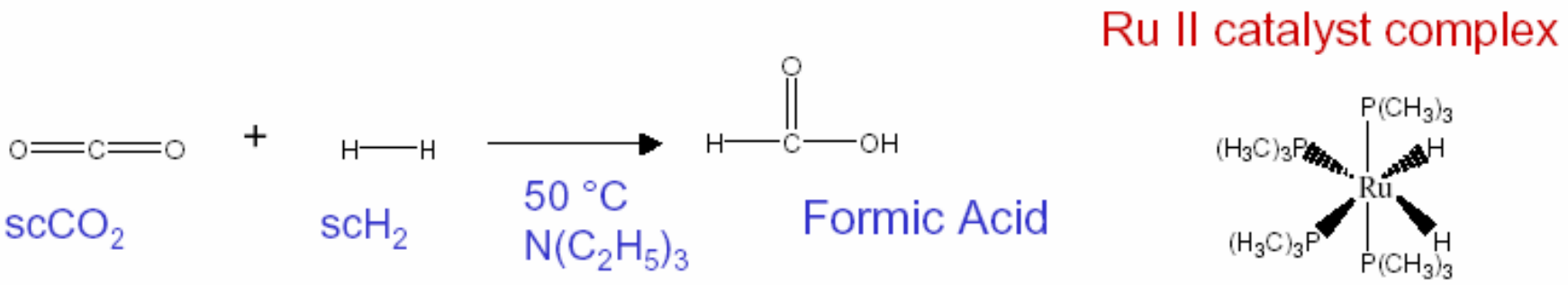
Tasmania lanceolata

Humulus lupulus



Alte aplicatii ale fluidelor supercritice

- Inlocuirea solventilor utilizati in litografie
- Polimerizarea fluoropolimerilor (lubrifianti pentru HDD) in CO_2 SC;
- Hidrogenarea catalitica a CO_2 SC ➔ obtinerea acidului formic:



Alte aplicatii ale fluidelor supercritice

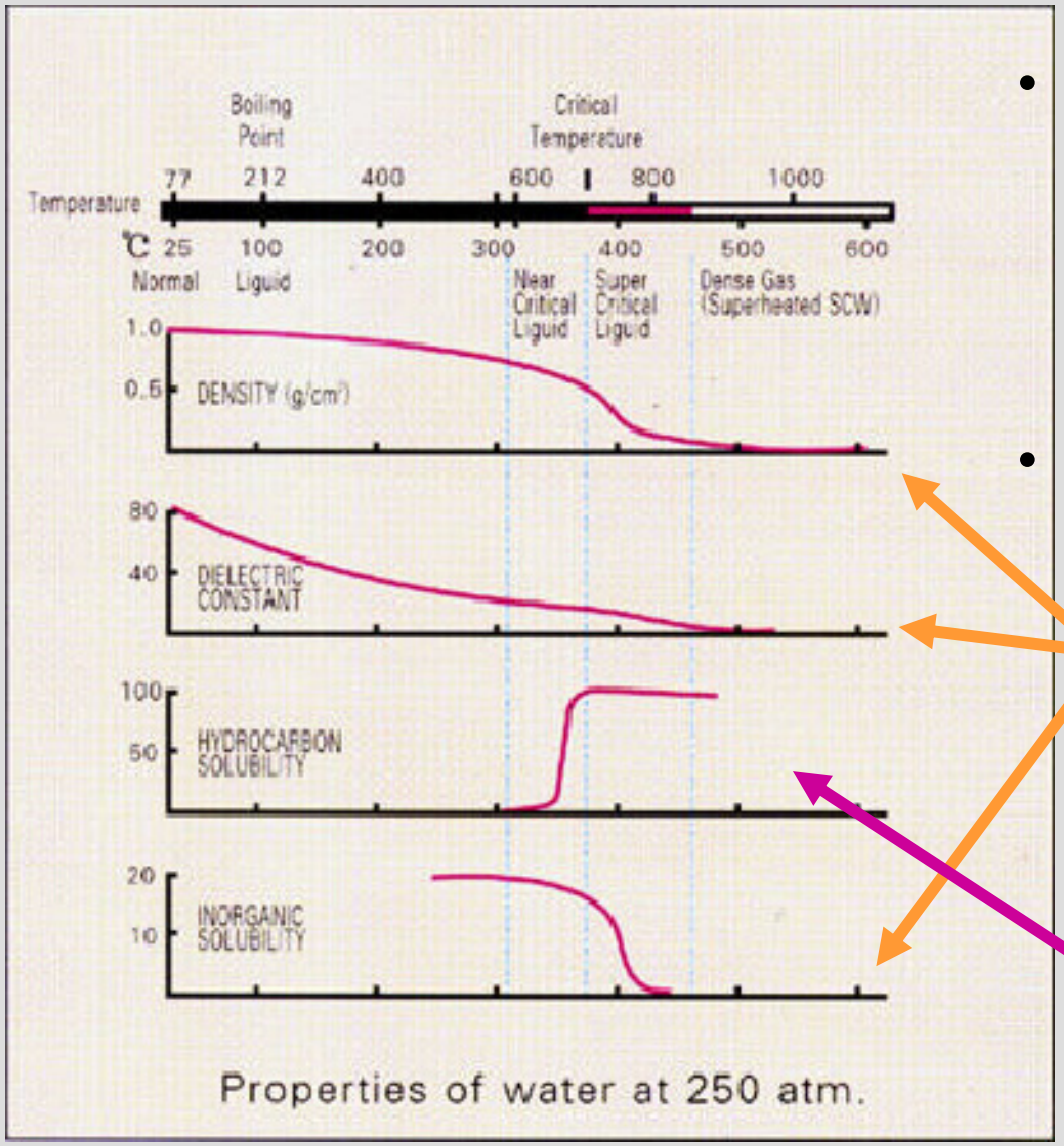
- Aditivi la polimeri: vopsirea textilelor, obtinerea materialelor reflectorizante;
- Uscarea: *obtinerea aerogelului de silice*
  - uscare fara vaporizare
  - fara expansie de volum
  - fara distrugerea structurii

Alte aplicatii ale fluidelor supercritice

- Inlocuirea solventilor potential cancerigeni din curatatoriile chimice (dry cleaning) cu CO_2 SC;
- Cromatografia cu FSC:
  - rezolutie inalta
  - sensibilitate ridicata
  - lucru la temperatura mai coborata decat in HPLC sau GC

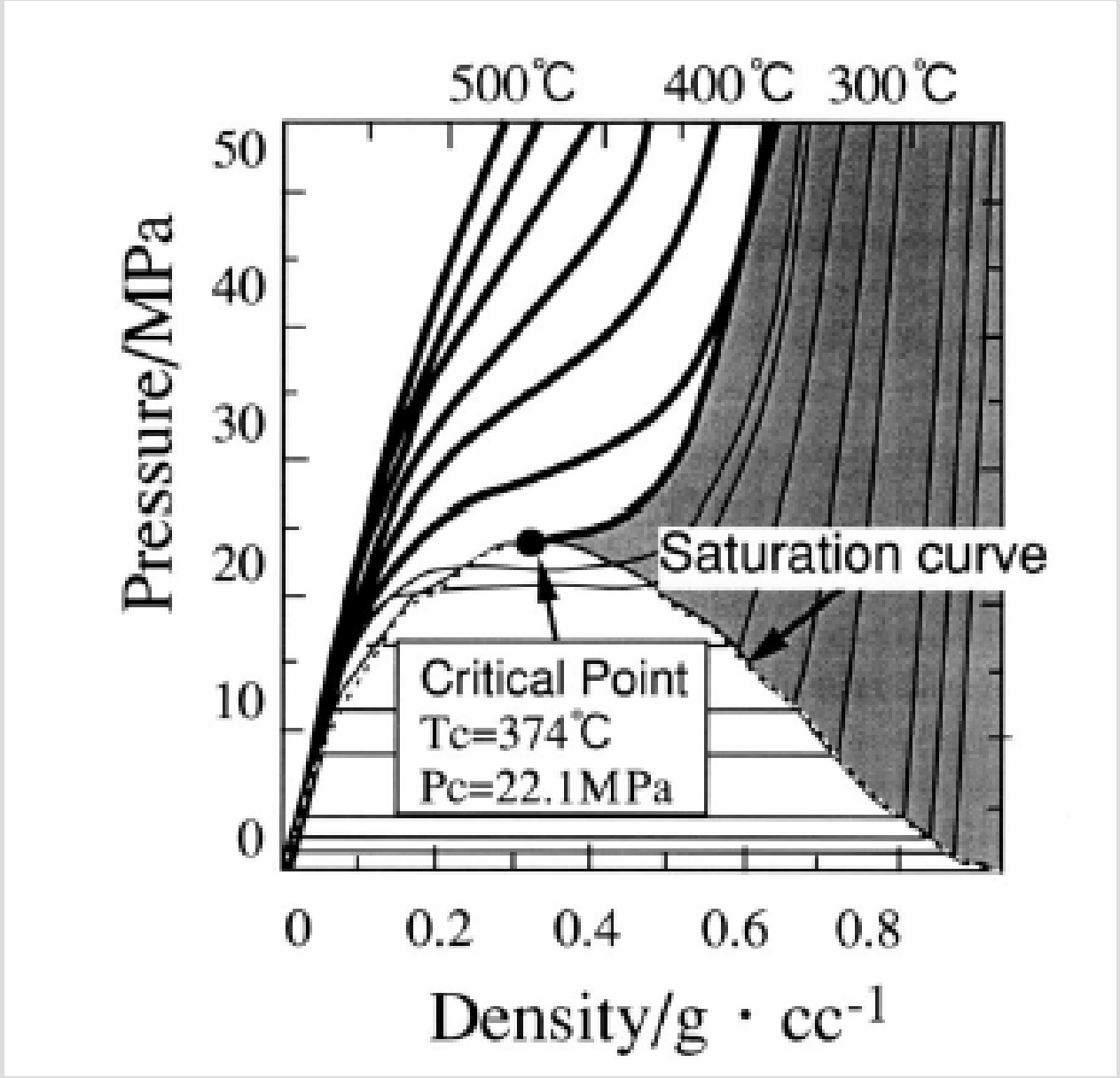
Nicotine and alkaloids in tobacco separated by SFC for analysis.

Alte aplicatii ale fluidelor supercritice



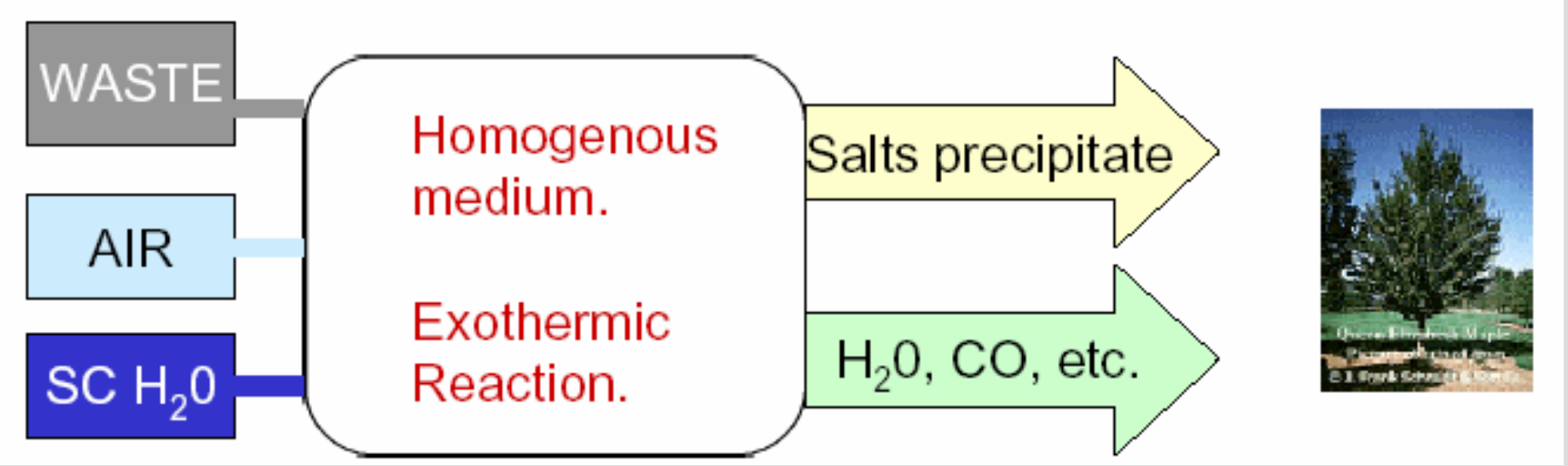
- Distrugerea reziduurilor organice prin **oxidare in apa supercritica**
- Apa in stare supercritica:
  - densitatea, constanta dielectrica si solubilitatea anorganicelor SCAD
  - solubilitatea hidro-carburilor CRESTE

Curbe densitate – presiune pentru apa



Alte aplicatii ale fluidelor supercritice

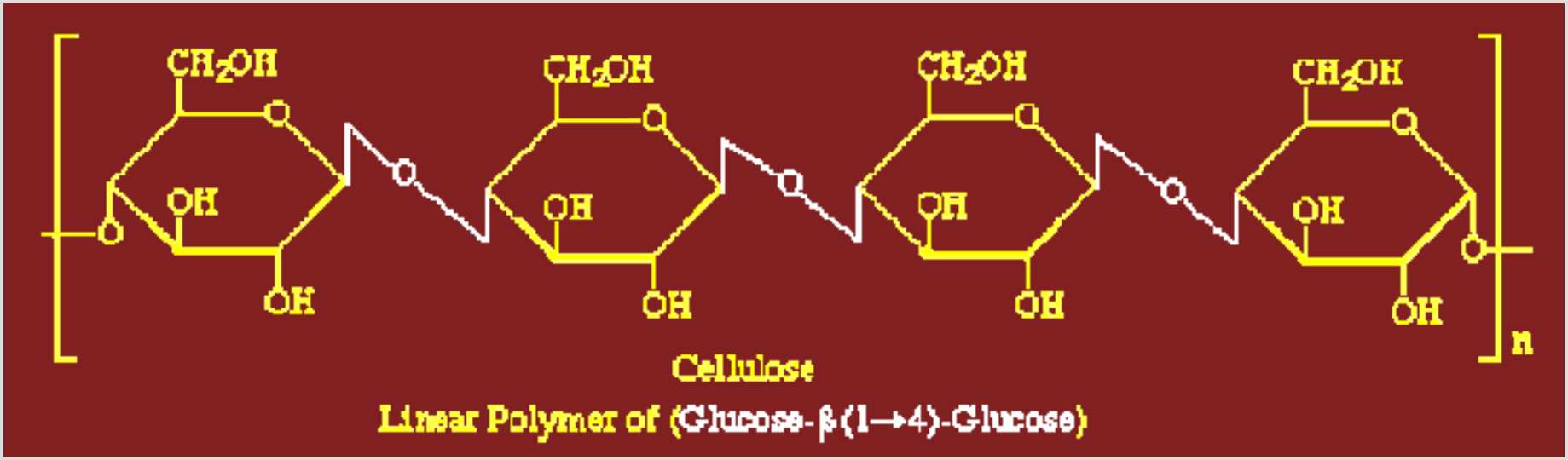
- La T > 550 °C, comp. organici toxici sunt miscibili cu apa, la fel si O_2 si H_2O_2;
- La T > 550 °C, majoritatea comp. anorganici sunt insolubili;



Alte aplicatii ale fluidelor supercritice

- **Gazeificarea biomasei cu apa supercritica**
  - componentele biomasei (celuloza, amidon, lignina), se dizolva si se scindeaza in apa SC;
  - in conditii corespunzatoare (~ 600 °C, ~ 35 MPa), gazeificarea este completa;
  - Produsii principali ai gazeificarii sunt: H_2, CH_4, CO_2.

Alte aplicatii ale fluidelor supercritice



$$C_6H_{10}O_5 + 7H_2O \longrightarrow 6CO_2 + 12H_2$$

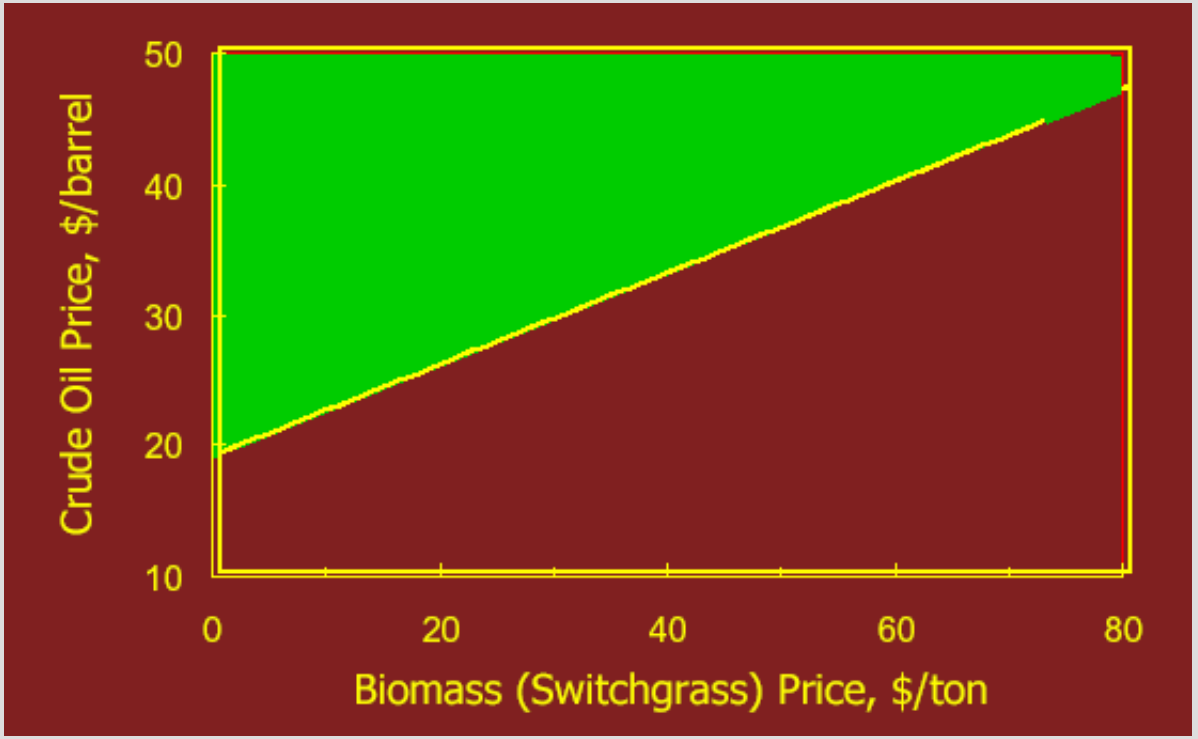
$$C_6H_{10}O_5 + H_2O \longrightarrow 3CO_2 + 3CH_4$$

water-gas-shift $\quad CO + H_2O \rightleftharpoons CO_2 + H_2$

methanation $\quad 2CO + 2H_2 \longrightarrow CH_4 + CO_2$

Alte aplicatii ale fluidelor supercritice

- In conditii mai blande, "aproape critice" (300 – 350 °C; 15 – 20 MPa), are loc lichefierea biomasei;
- Biomasa lichefiata = titei din biomasa;
- In conditii corespunzatoare se pot forma zaharuri, acizi organici, alte produse valoroase.



Alte aplicatii ale fluidelor supercritice

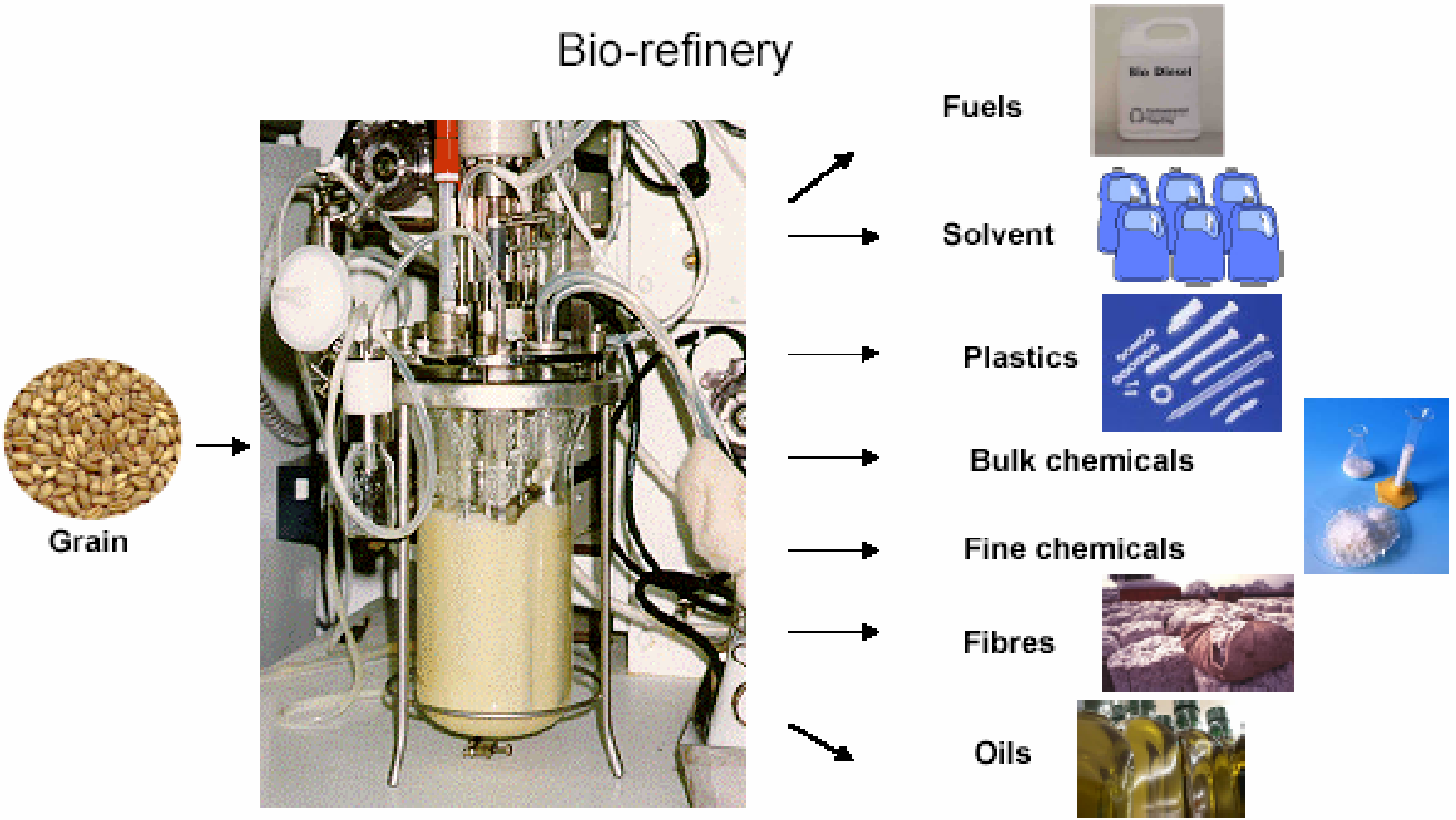


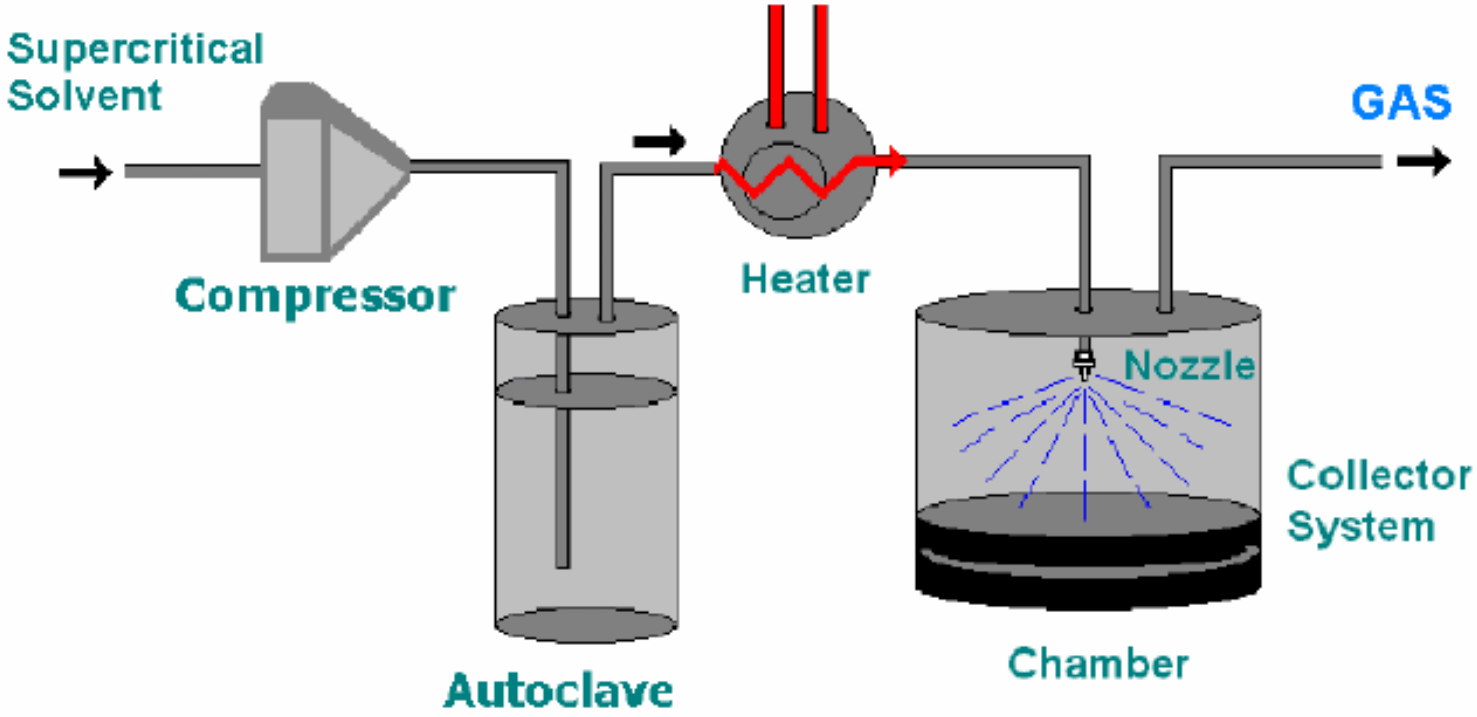
Fig. 1: Examples of products that can be derived from biomass

Alte aplicatii ale fluidelor supercritice

- Expansiunea Rapida a Solutiilor SuperCritice (ERSSC);
- Procese de Cristalizare Gaz Antisolvent (CGAS) si Solvent AntiSolvent (CSAS);
- Separarea Particulelor din Solutii Suprasaturate (SPSS).

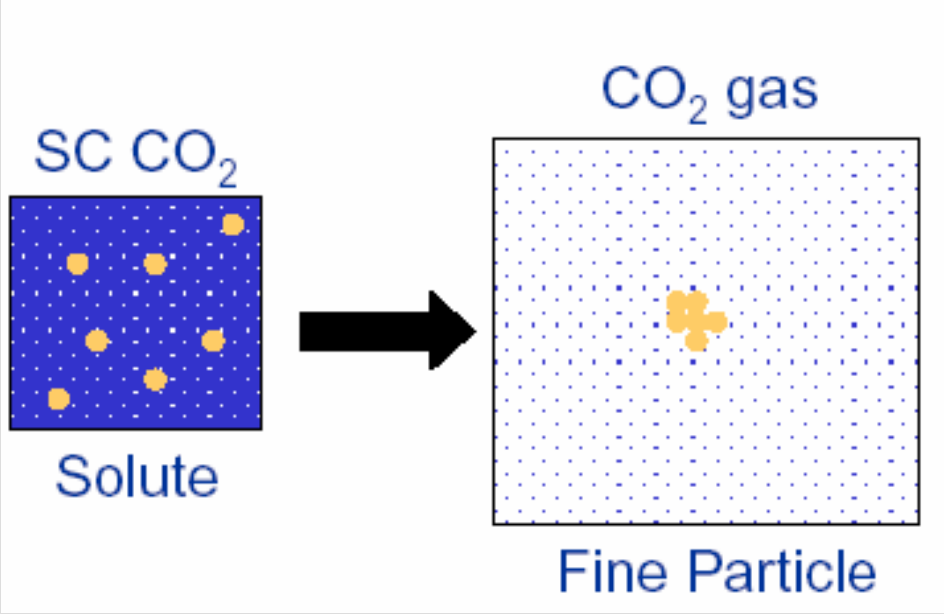
Expansiunea Rapida a Solutiilor SuperCritice (ERSSC)

The Use of Supercritical Fluid Extraction Technology in Food Processing
R.S. Mohamed and G.A. Mansoori
Featured Article - Food Technology Magazine, June 2002
The World Markets Research Centre, London, UK



Expansiunea Rapida a Solutiilor SuperCritice (ERSSC)

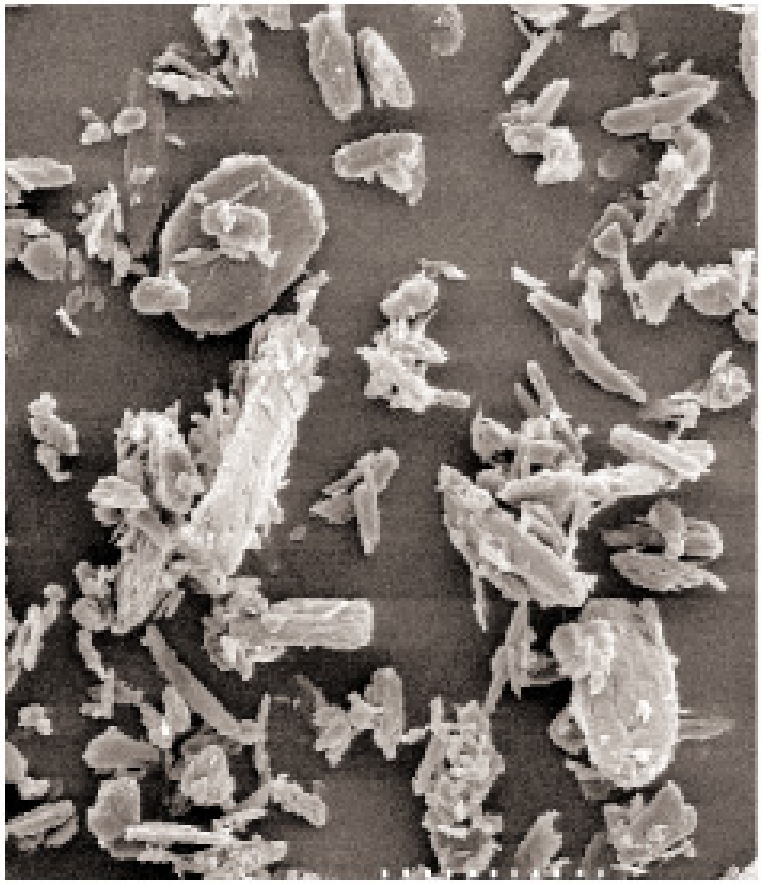
- Solutul se dizolva in CO_2 SC;
- Solutia este expandata la P atm.;
- Solubilitatea scade de 10^6 ori;
- Se creaza suprasaturatia si nucleatia;
- Rezulta particule uniforme, cu dimensiuni controlabile.



Expansiunea Rapida a Solutiilor SuperCritice (ERSSC)

- ACID NICOTINIC - imagini la microscopul electronic:

obtinut pe cale clasica



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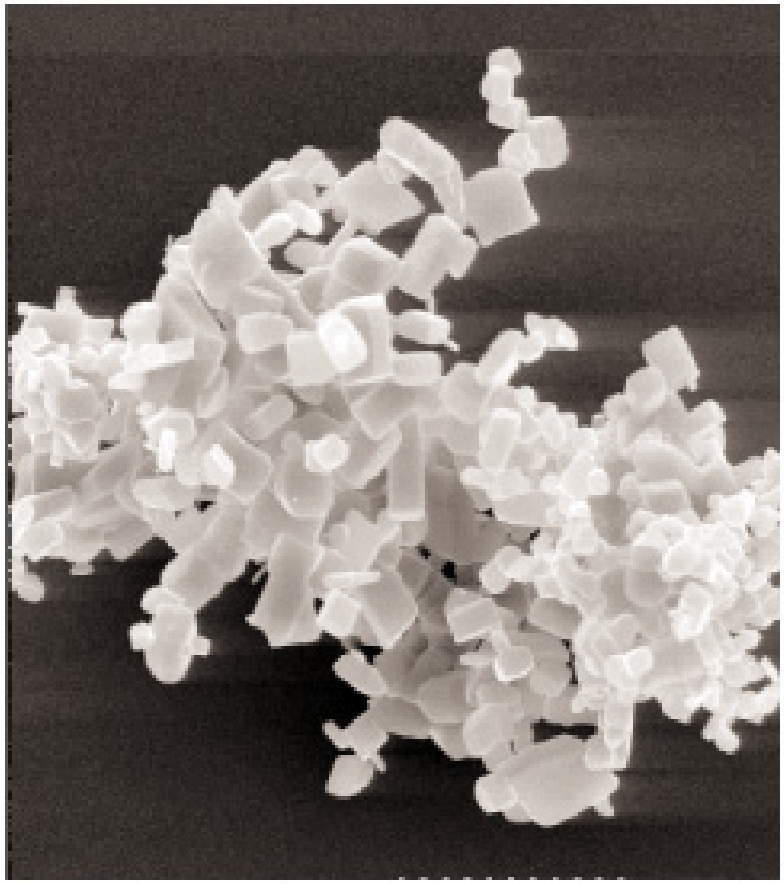
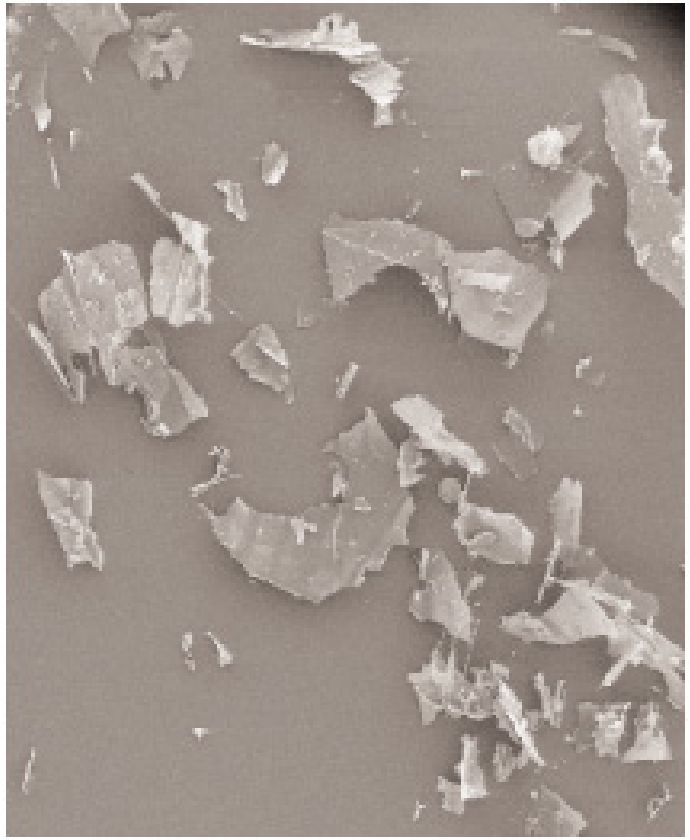


Expansiunea Rapida a Solutiilor SuperCritice (ERSSC)

- LYSOZIMA - imagini la microscopul electronic:

obtinuta prin crioconcentrare



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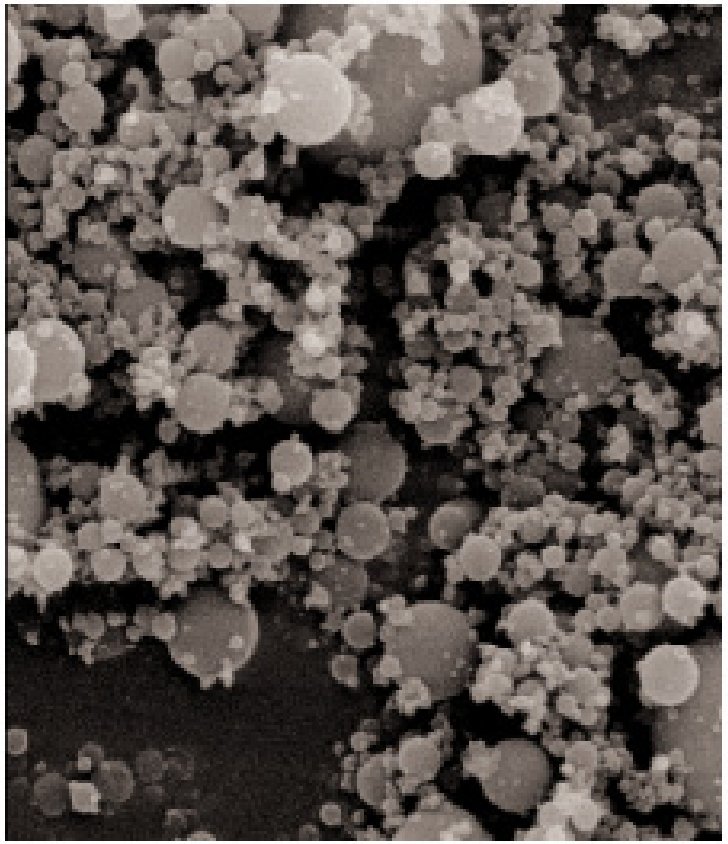
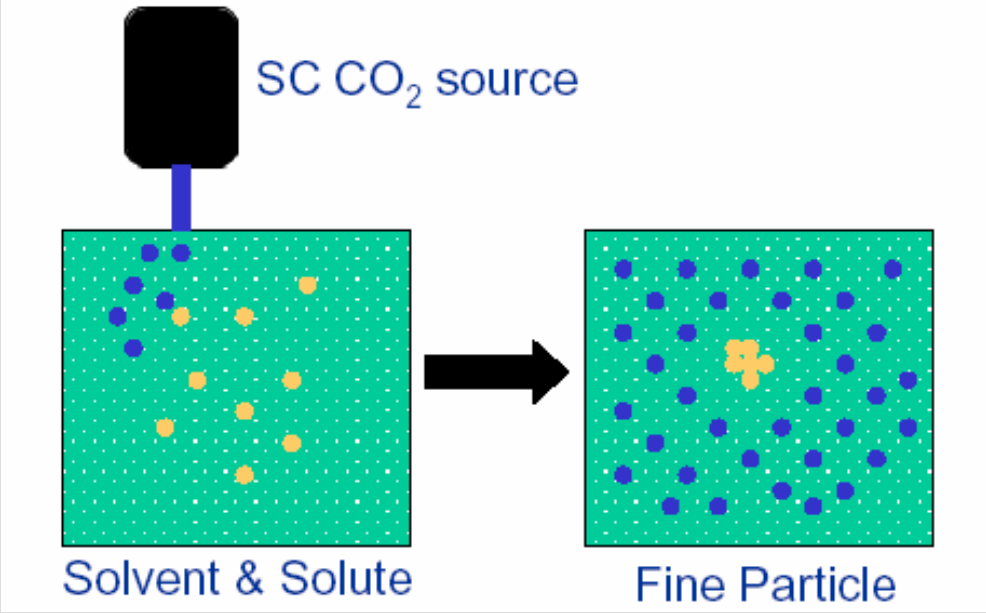
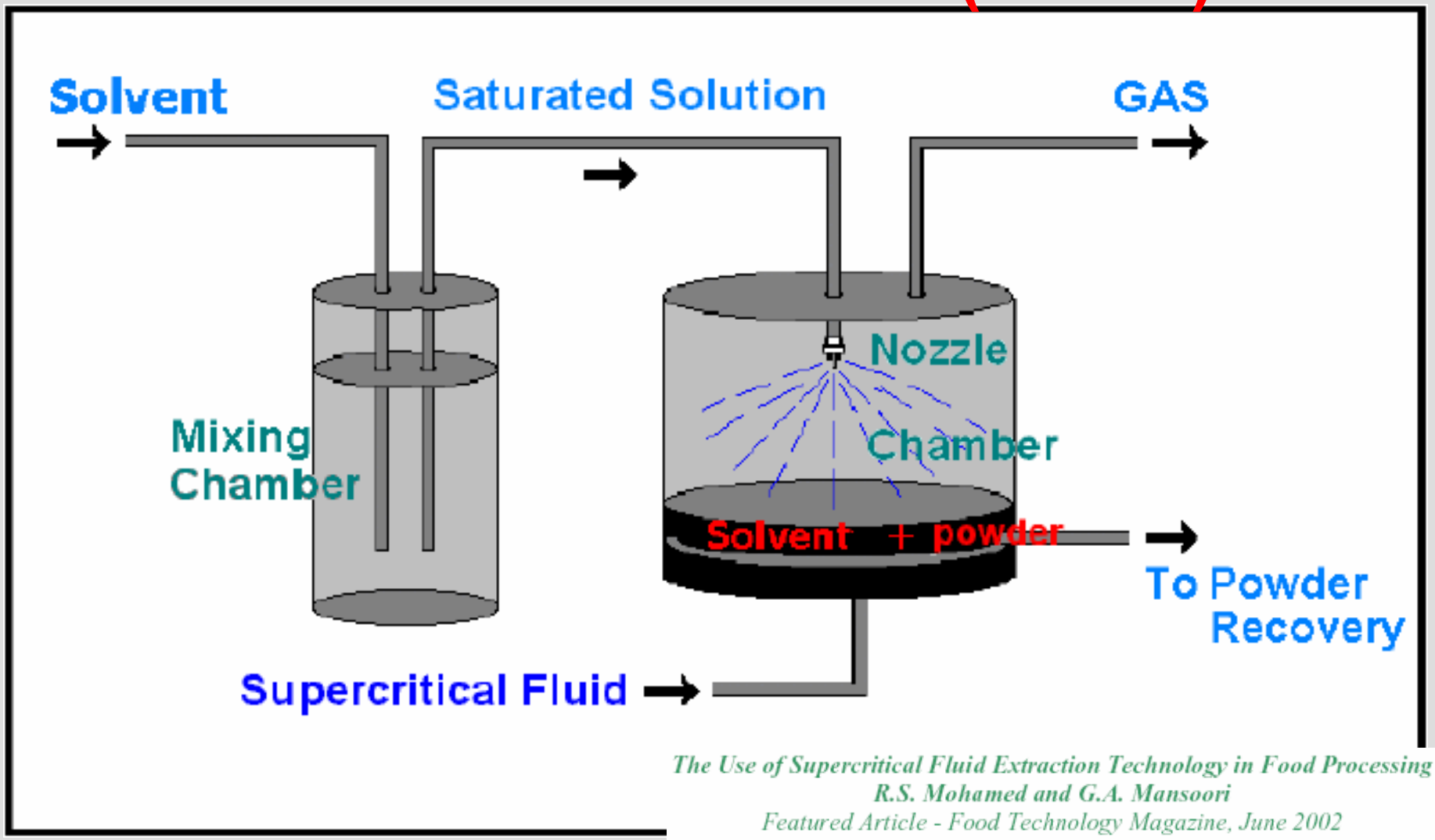


Cristalizarea Gaz Antisolvent (CGAS) si Solvent AntiSolvent (CSAS)

- Compusul (medicament) se dizolva in solventul purtator;
- Solventul purtator este partial miscibil cu CO_2;
- Amestecarea solventului purtator cu CO_2 SC provoaca precipitarea compusului.



Cristalizarea Gaz Antisolvent (CGAS) si Solvent AntiSolvent (CSAS)



The Use of Supercritical Fluid Extraction Technology in Food Processing
R.S. Mohamed and G.A. Mansoori
Featured Article - Food Technology Magazine, June 2002
The World Markets Research Centre, London, UK

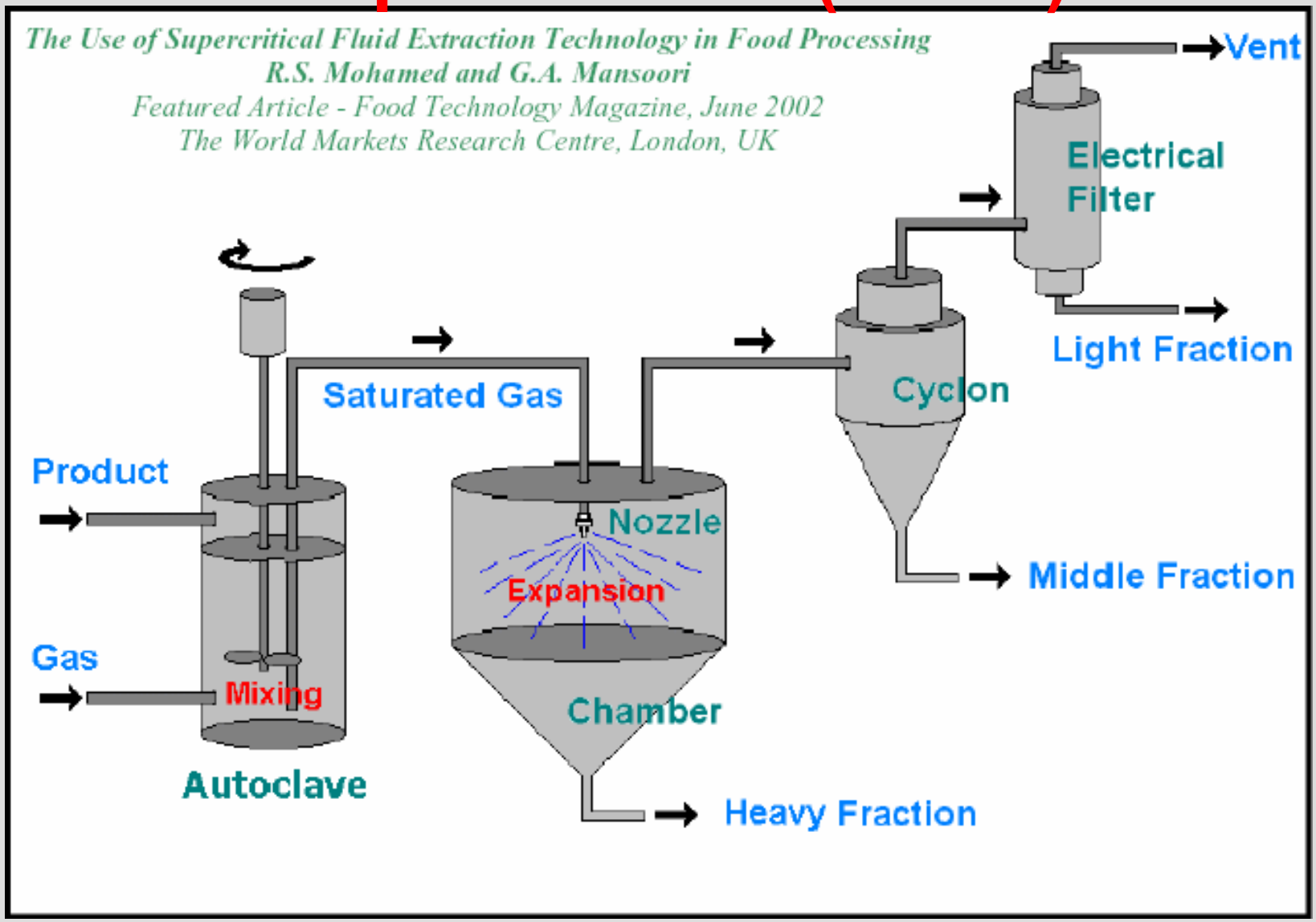
Aplicatii ale ERSSC, CGAS, CSAS

- Microincapsularea aromelor si parfumurilor (volatile, termolabile, sensibile la oxidare, scumpe)
  - eliberarea aromelor in timpul prepararii hranei cu microunde;
  - protejarea aspartamului in timpul gatirii;
  - protectia la oxidare a uleiurilor si esentelor;
  - mascarea gustului de KCl;
  - reducerea amestecarii aromelor;
  - produse finite necontaminate cu solvent;
  - comp. active nu se degradeaza ca la uscarea prin atomizare

Aplicatii ale ERSSC, CGAS, CSAS

- Aplicatii farmaceutice:
  - medicamentele sub forma de aerosoli necesita particule uniforme, de mici dimensiuni;
  - este necesara obtinerea de pro-duse sterile;
  - CO_2 inlocuieste conditiile aseptice asigurate cu eter etilic.

Separarea Particulelor din Solutii Suprasaturate (SPSS)



Separarea Particulelor din Solutii Suprasaturate (SPSS)

- Solutia produsului se amesteca cu CO_2 SC;
- Amestecul este pulverizat la P si T controlate intr-un recipient in care are loc formarea particulelor solide;
- Picaturile formate sunt in general mai mici decat cele obtinute prin alte metode;
- Procesul permite obtinerea nanoparticulelor de substante insolubile in CO_2 SC.

Aplicatii ale ERSSC, CGAS, CSAS

Drug	Cosolvent/ solution	Process	Mean particle size (μm)
Lovastatin	3% Methanol	RESS	0.1-0.3
Stigmasterol	3% Methanol	RESS	0.05-3
Salicylic acid	3% Methanol	RESS	2-20
Theophylline	3% Methanol	RESS	0.4
Estradiol	3% Methanol	SFN	<1
Progesterone	3% Methanol	SFN	<1
Testosterone	3% Methanol	SFN	<1
Insulin	DMSO	SAS	1-5
Lysozyme	DMSO	SAS	1-5
Trypsin	DMSO	SAS	1-5
Hydrocortisone	DMSO	PCA	0.2-1
Dexamethasone	Acetone/Ethanol	GAS	<1
Prednisolone	-	SFN	<5

RESS = ERSSC
SAS = CSAS
SFN = nucleatie cu fluide supercritice
PCA = precipitare cu fluid antisolvent comprimat
GAS = CGAS

CONCLUZII

- Fluidele supercritice au proprietati unice:
  - difuzivitate ridicata;
  - tensiune superficiala scazuta;
  - constanta dielectrica joasa;
  - densitate continuu variabila.
- Sunt neinflamabile, netoxice, ieftine, nu necesita conditii speciale de depozitare;
- Reprezinta o alternativa "verde" pentru solventii clasici in:
  - curatire
  - extractie
  - sinteza

CONCLUZII

- **Fluidele supercritice** permit fabricarea unor materiale special structurate, care nu pot fi obtinute prin metode conventionale;
- Deschid noi drumuri in procesele de:
  - extractie
  - separare cromatografica
  - eliminare a deseurilor toxice.