EKC 316
Separation Processes

Supercritical Fluid Extraction

Course Learning Objectives

- Apply the principles and theory of super critical fluid extraction.
- Develop design strategies.

Principles and theory:

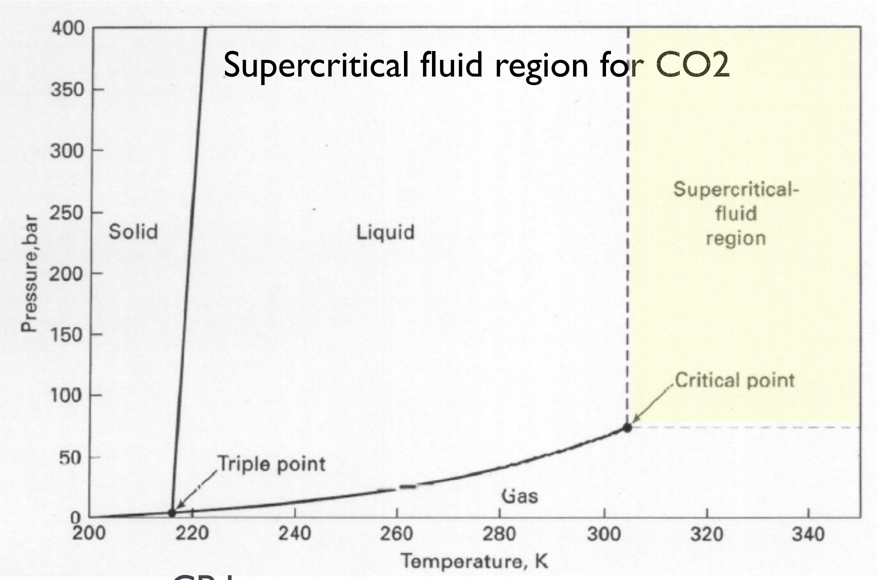
- Supercritical Fluid Extraction: Physical and transport properties of supercritical fluid,
- Phase diagrams of supercritical fluid and estimation of solid solubility at high pressure,
- Type of supercritical fluids, industrial applications of SFE: SFE of essential oils.

Course Strategies: Explain the supercritical fluid phase diagram and applications of supercritical fluid extration in industry.

Course Activities: Lectures in class; Discussions; Tutorial; Test

Physical and transport properties of supercritical fluid

- Supercritical fluid is gas or liquid above its critical T and P as shown in the phase diagram.
- The critical point is marked at the end of the gas-liquid equilibrium curve, and the highlighted area indicates the supercritical fluid region.
- By using isobaric changes in temperature with isothermal changes in pressure, it is possible to convert a pure component from a liquid to a gas (and vice versa) via the supercritical region without incurring a phase transition.
- SCF behaves as a very mobile liquid. The solubility behavior approaches that of the liquid phase while penetration into a solid matrix is facilitated by the gas-like transport properties.
- The accented region denotes supercritical fluid space where gases show tendency to dissolve materials.

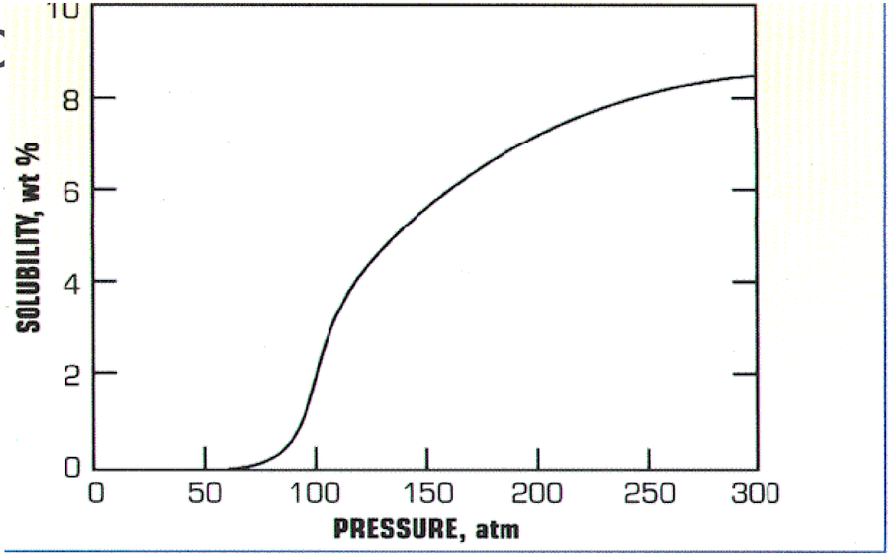


Physical and transport properties of supercritical fluid

- Only 1 phase exists in the supercritical region. SCF is neither a gas nor a liquid and is best described as intermediate to the two extremes. This phase retains solvent power approximating liquids as well as the transport properties common to gases.
- A comparison of typical values for density, viscosity and diffusivity of gases, liquids, and SCFs is presented in below table.
- In 1879, Hannay and Hogarth, reported that supercritical fluids have a P-dependent dissolving ability. The dissolving ability is higher at the higher P.
- A few years later, Eduard Buchner (1907 Nobel Prize winner) measured the solubility of a model compound, naphthalene, in supercritical carbon dioxide. Supercritical fluids activity of naphthalene is still studied today.

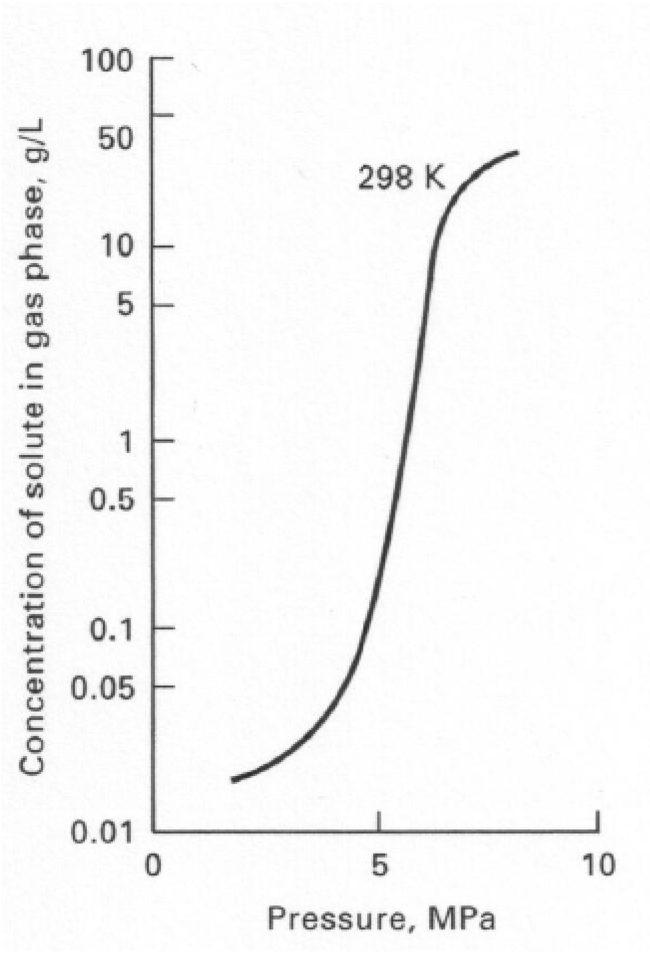
Property	Density (kg/m3)	Viscosity (cP)	Diffusivity (mm2 /s)
Gas	1	0.01	1-10
SCF	100-800	0.05-0.1	0.01-0.1
Liquid	1000	0.5-1.0	0.001

Physical and transport p supercritical fluid

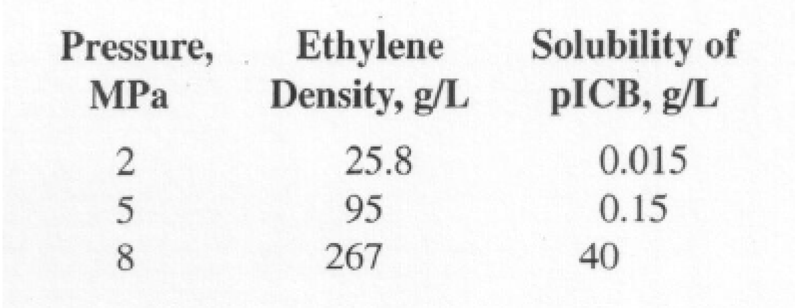


- The solubility of naphthalene in supercritical carbon dioxide is shown in above figure.
- At low P, its solubility is essentially nil.
- As the P of the gas is increased to above Pc of carbon dioxide (73 atm), the solubility increases dramatically for many compounds including naphthalene.
- For example, at 200 atm and 45°C, the solubility is 7%. Soluble components are extracted from a substrate by a high pressure gas, and the extracted components that have been dissolved in the gas are precipitated from the gas when the pressure is reduced, for example, across a pressure reduction valve.

Physical and transport properties of supercritical fluid



- The figure shows the effect of pressure on solubility of p-iodochlorobenzene (pICB) in supercritical ethylene at 298 K which is 1.05 times of Tc.
- The solvent power of the compressed gas can undergo an enormous change in the vicinity of its critical point.
- The explanation lies in the change that occurs to the solvent density while the solubility of the solute increase.
- As P increases, closer packing of the solvent molecules allows them to surround and trap solute molucules.
- The phenomenon is most dramatic at reduced tempreratures 1.01 to 1.12.



Pressure, MPa	Ethylene Density, g/L	Solubility of pICB, g/L
2	25.8	0.015
5	95	0.15
8	267	40

Physical and transport properties of supercritical fluid

- Besides that, the diffusivity of solute molecules in a near critical fluid is 1 or 2 magnitude higher than in a normal liquid solvent.
- In addition, the viscosity of the supercritical is about an order of magnitude less than that of a normal liquid solvent.
- Mechanism for solubilization of solutes in SCF:
- If there is no interaction between solute and solid phase, the process is dissolution of solute in suitable solvent.
- If there is interaction between solute and solid, extraction is desorption. Adsorption isotherm of solute on the solid in presence of solvent determines the equilibrium.
- Swelling of solid phase by the solvent accompanied by extraction of entrapped solutes through the first two mechanisms.
- Reactive extraction. Insoluble solutes react with solvent and products are soluble and hence extractable. For example, lignin extraction from cellulose.

Physical and transport properties of supercritical fluid

- Simple expansion of SCF leads to lowering in solubility capacity of it. Thus, dissolved solutes are separated.
- They have liquid like density but superior mass transfer behaviour compared to liquids due to high diffusivity and low surface tension so that they can penetrate into the porous structure of solid matrix to release the solute.
- The rates of extraction and phase separation can be significantly faster than for conventional extraction processes. Furthermore, the extraction conditions can be controlled to effect a selected separation.
- Supercritical fluid extraction is known to be dependent on the density of the fluid that in turn can be manipulated through control of the system pressure and temperature.
- The dissolving power of a SCF increases with isothermal increase in density or an isopycnic (i.e. constant density) increase in temperature. In practical terms this means a SCF can be used to extract a solute from a feed matrix as in conventional liquid extraction.
- However, unlike conventional extraction, once the conditions are returned to ambient the quantity of residual solvent in the extracted material is negligible.

Physical and transport properties of supercritical fluid

- SCF extraction is that the solubility of a given compound (solute) in a solvent varies with both temperature and pressure. At ambient conditions (25°C and 1 bar) the solubility of a solute in a gas is usually related directly to the vapor pressure of the solute and is generally negligible.
- In a SCF, however, solute solubilities of up to 10 orders of magnitude greater than those predicted by ideal gas law behavior have been reported.
- The dissolution of solutes in supercritical fluids results from a combination of vapor pressure and solute-solvent interaction effects. The impact of this is that the solubility of a solid solute in a supercritical fluid is not a simple function of pressure.
- Although the solubility of volatile solids in SCFs is higher than in an ideal gas, it is often desirable to increase the solubility further in order to reduce the solvent requirement for processing.
- The solubility of components in SCFs can be enhanced by the addition of a substance referred to as an entrainer, or cosolvent. of the resulting mixture considerably.

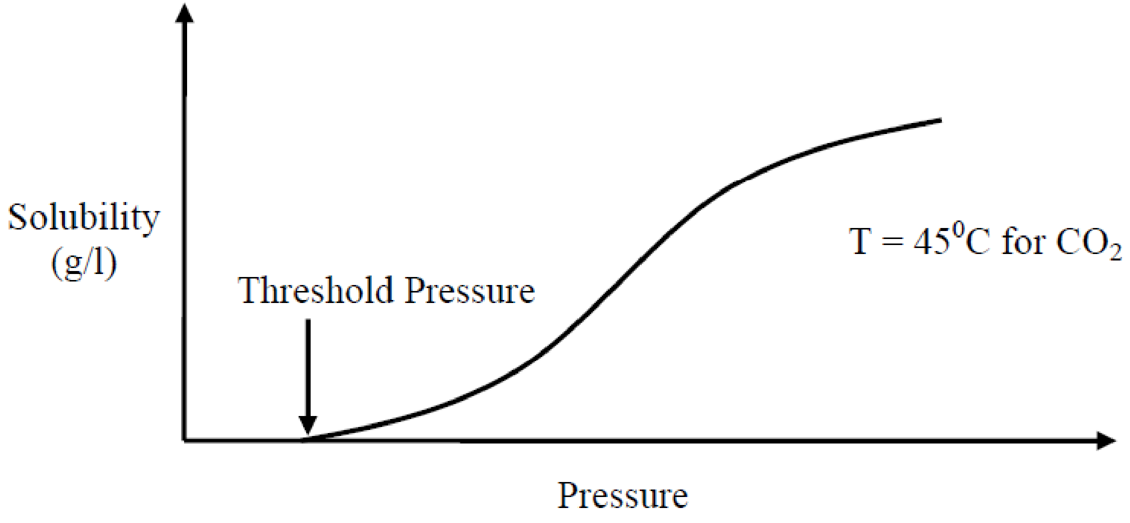
Physical and transport properties of supercritical fluid

- The volatility of this additional component is usually intermediate to that of the SCF and the solute. The addition of a cosolvent provides a further dimension to the range of solvent properties in a given system by influencing the chemical nature of the fluid.
- Cosolvents also provide a mechanism by which the extraction selectivity can be manipulated. The commercial potential of a particular application of SCF technology can be significantly improved through the use of cosolvents. A factor that must be taken into consideration when using cosolvents, however, is that even the presence of small amounts of an additional component to a primary SCF can change the critical properties of the resulting mixture considerably.

Physical and transport properties of supercritical fluid

Important Parameters for SCF Extraction

- Threshold pressure: Pressure at which miscibility of solute starts. shows typical solubility curve of a material at a particular temperature.
- Pressure at which solute reaches its maximum solubility.
- Knowledge of physical properties of solutes (particularly, melting points). Solutes are dissolved better in liquid state.



Typical solubility curve of a material at a particular temperature.

SCF Extraction

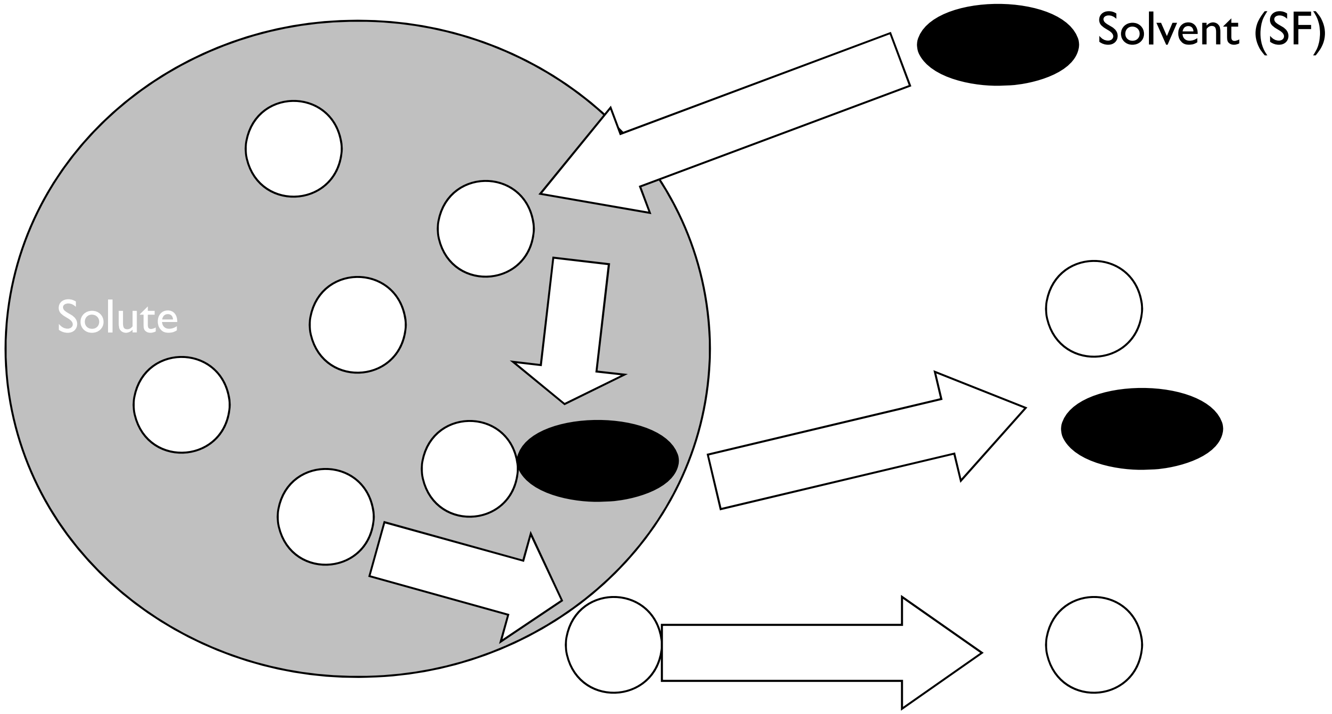
Types of SCF Extraction

- Solid-SF extraction
  - Similar to solid-liquid extraction (leaching)
  - Examples:
    - Removal of caffeine from coffee beans
    - Polymer fractionation
    - Extraction of flavours from rose petals
    - Extraction of essential oils from natural products
- Liquid-SF extraction
  - Similar to liquid-liquid extraction
  - Examples:
    - Increasing ethanol concentration in aqueous solution
    - Removal of alcohol from beer

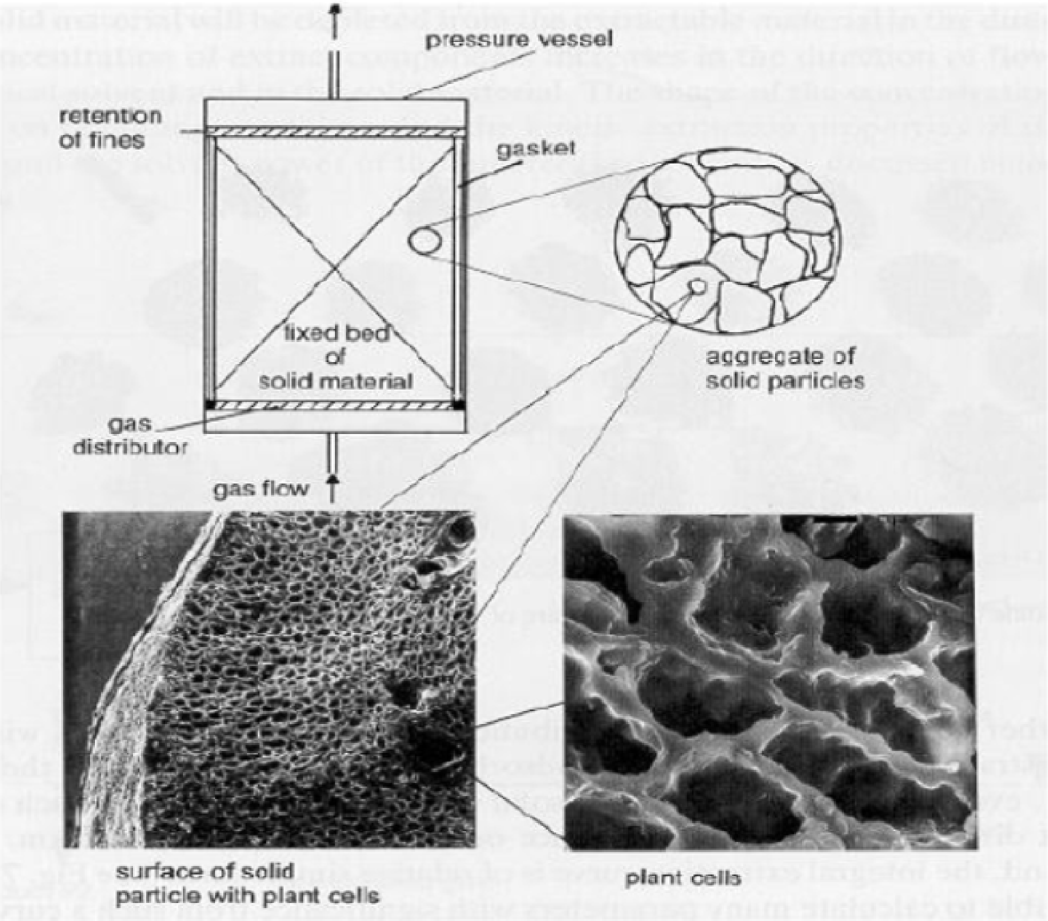
SCF Extraction

Solid-SF extraction

- Diffusivity of solvent molecules in a SF approach gaseous state diffusivity
- Solute diffusivity within a SF approaches that shown in gaseous phase

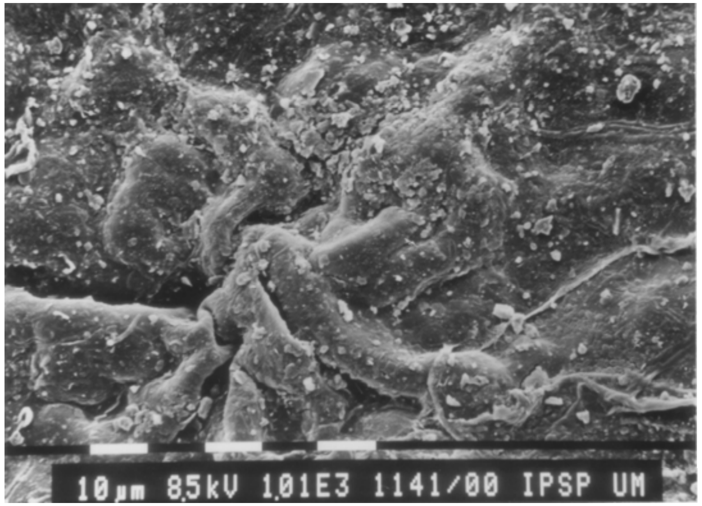


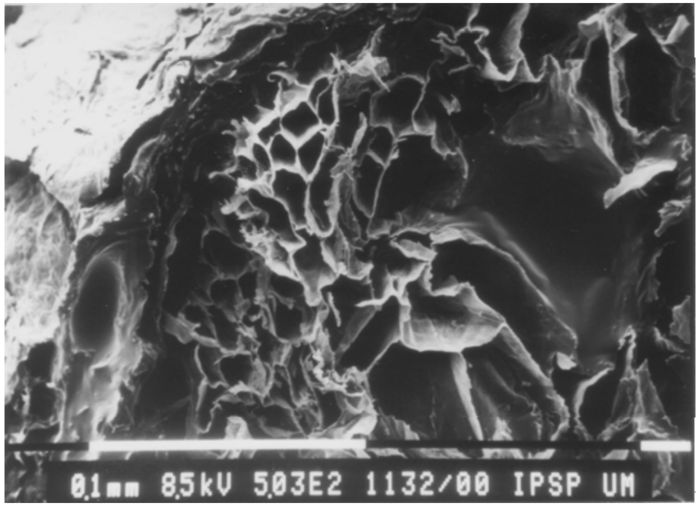
SCF Extraction

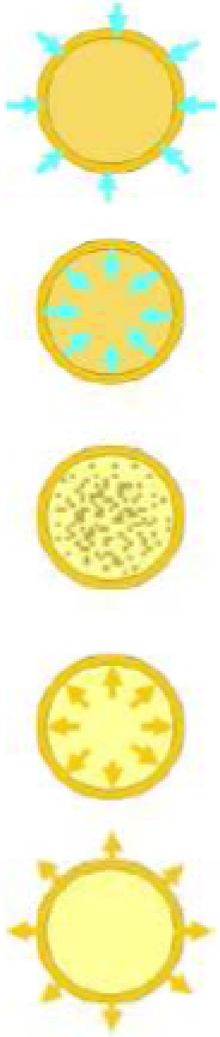


Plants differ in:
- Materials structure
- Harvesting period
- Treatment after harvesting age
- Pretreatment before extraction
- Particle size and shape
- Initial distribution
- etc

SCF Extraction







Diffusion of solvent through the film around the solid particle,

Streaming of solvent into the pores of the solid particle,

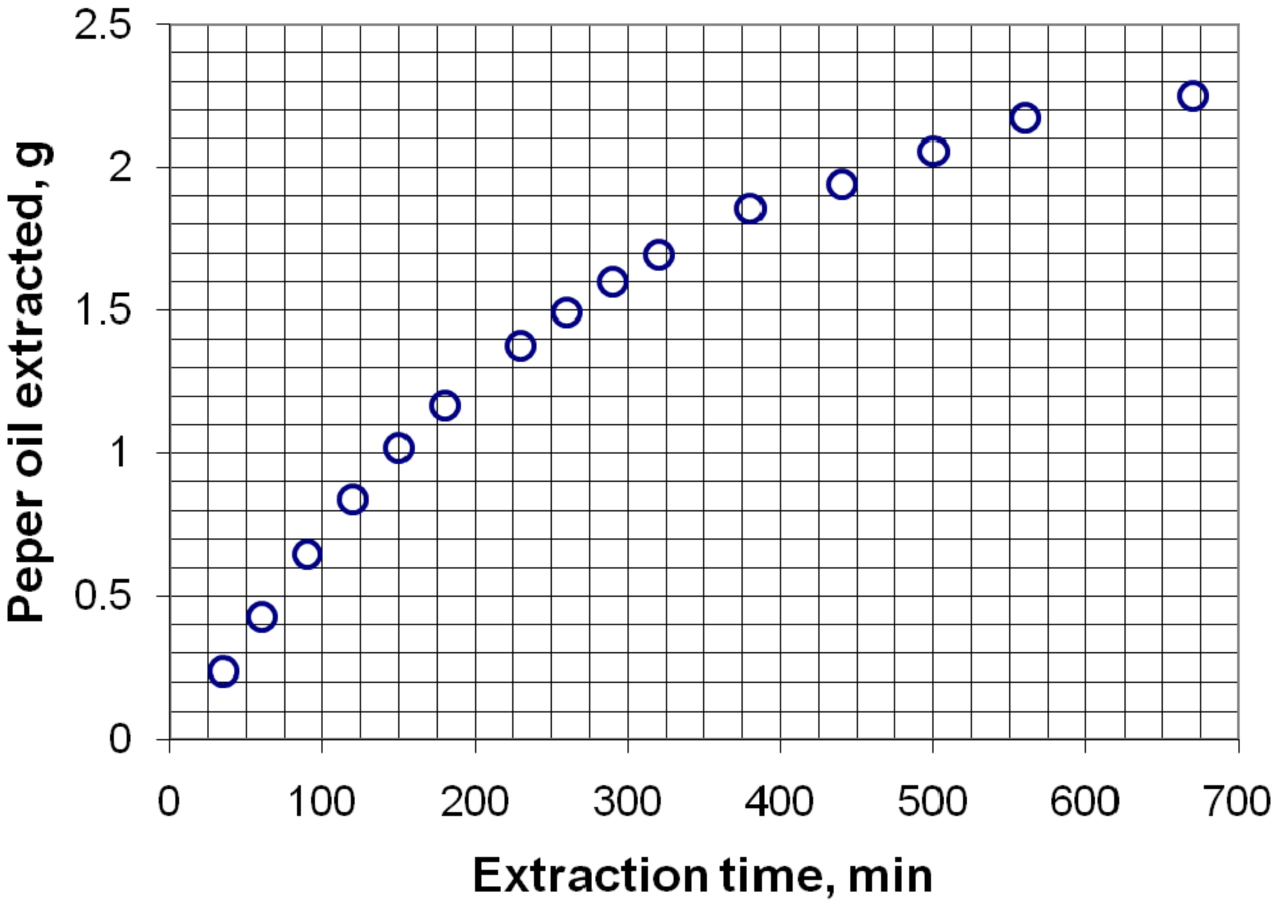
Solution of the soluble components,

Diffusion of the solute to the surface of the solid particle,

Mass transfer from the surface to the fluid bulk phase.

SCF Extraction

Typical extraction curve



SCF Extraction

Empirical Model for Solid-SF Extraction

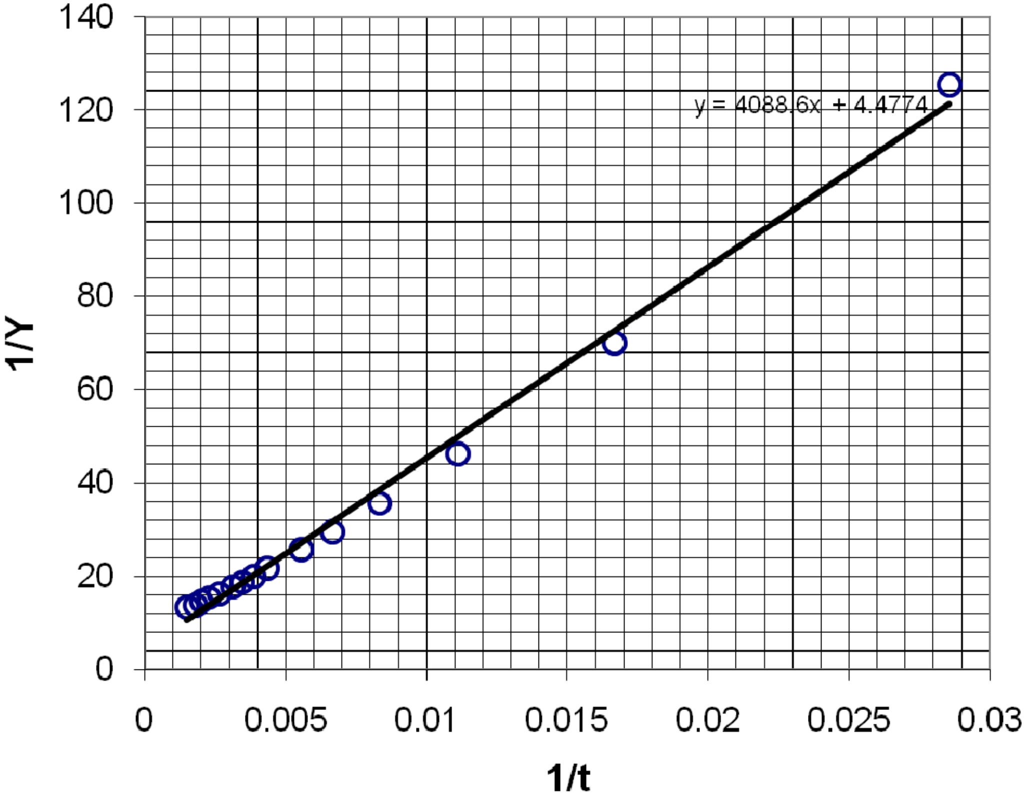
The simple empirical equation proposed by Naik et al. [1989] has been used to describe the experimental data from this study. They represented the extraction yield (Y) against the extraction time (t) in terms of a Langmuir-like-empirical equation:

$$Y = \frac{Y_\infty t}{B + t}$$

in which, Y is the specific amount of solute (g extract/g solute-free feed), Y_∞ is the maximum yield after an infinite extraction, t is the extraction time, and Y_∞/B is the initial slope of the specific oil yield as a function of time.

SCF Extraction

In fact both the value of B and Y_∞ can be determined through linearization of the previous equation into general linear equation form, Y=mX + C, by simply inverse the mentioned equation

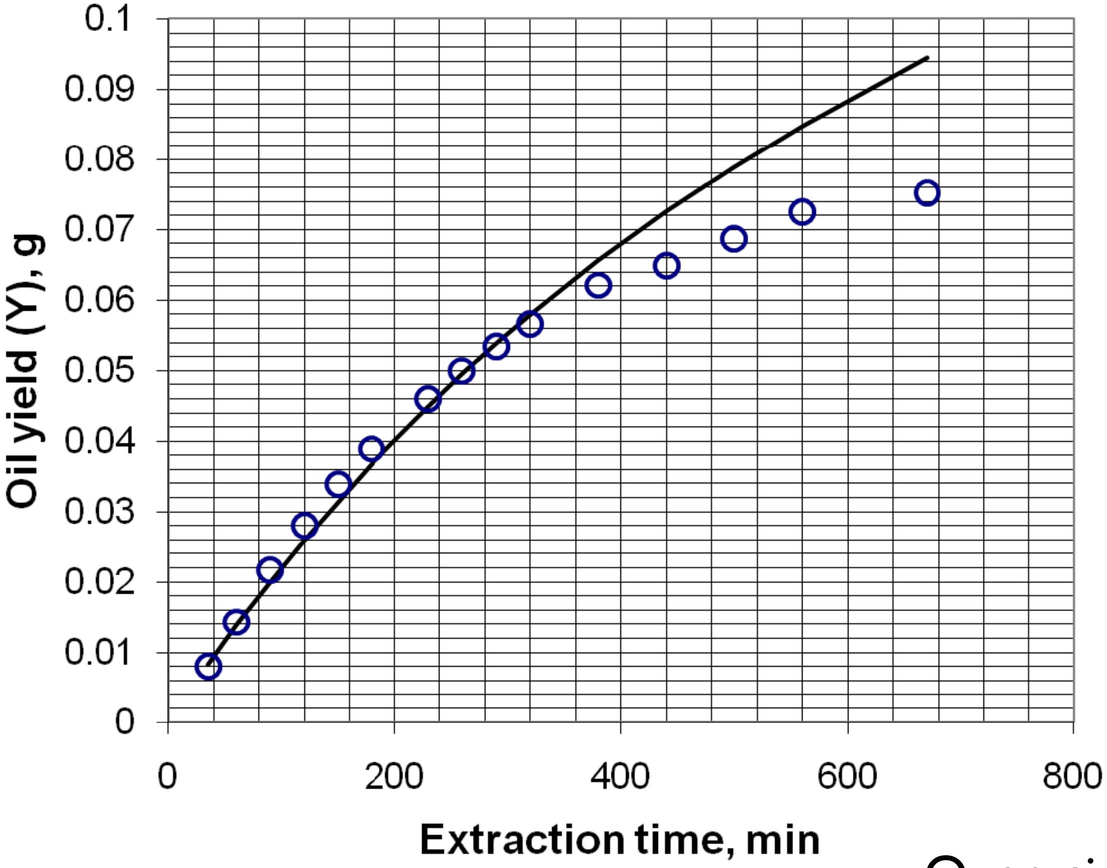


$$\frac{1}{Y} = \left(\frac{B}{Y_\infty}\right)\frac{1}{t} + \frac{1}{Y_\infty}$$

Here Y_∞ = 0.2233, and
B = 913.1639

SCF Extraction

Comparison of Y_{model} and Y_{exp}

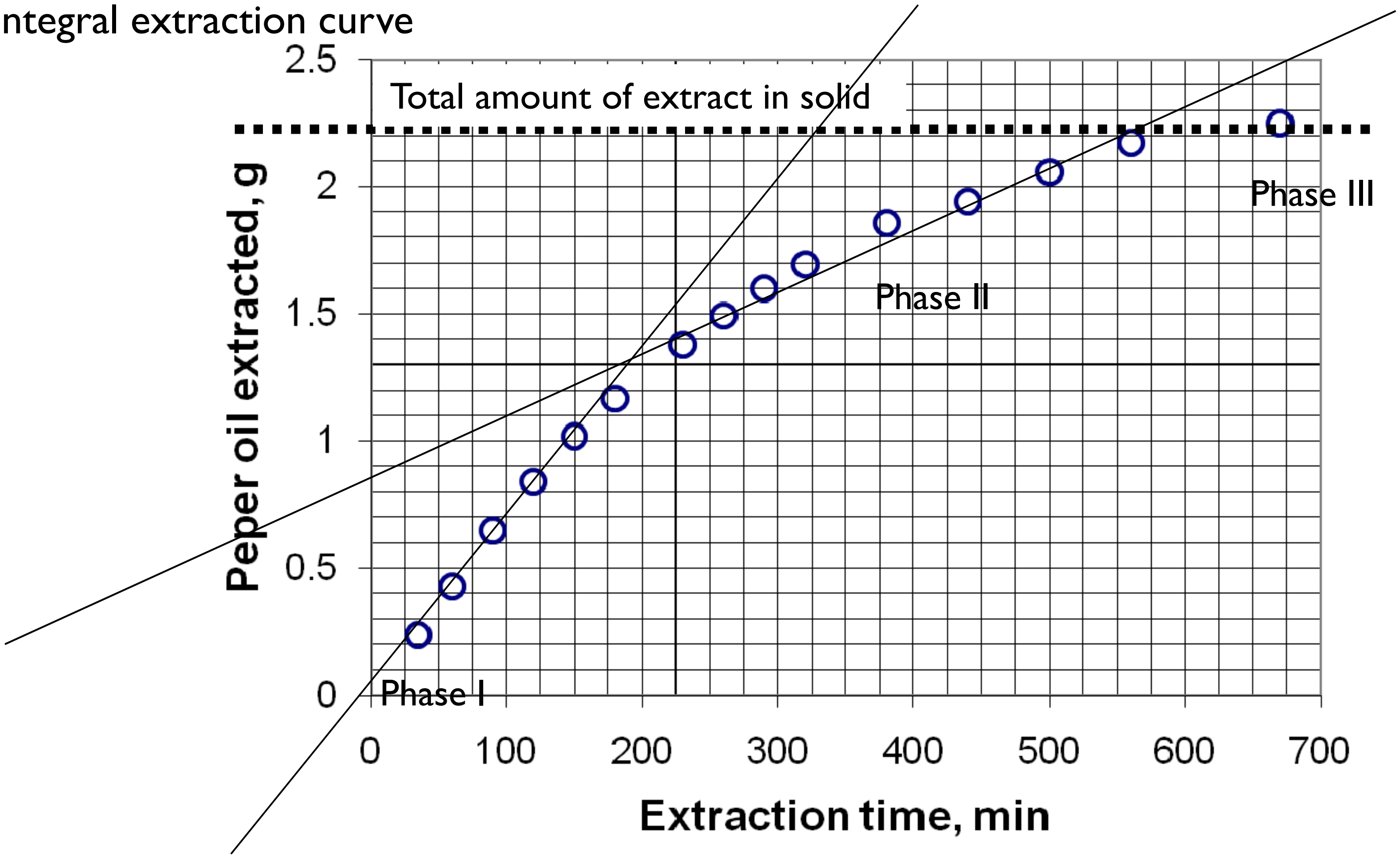


Open circle – experiment

Straight line – emperical model

SCF Extraction

Integral extraction curve



SCF Extraction

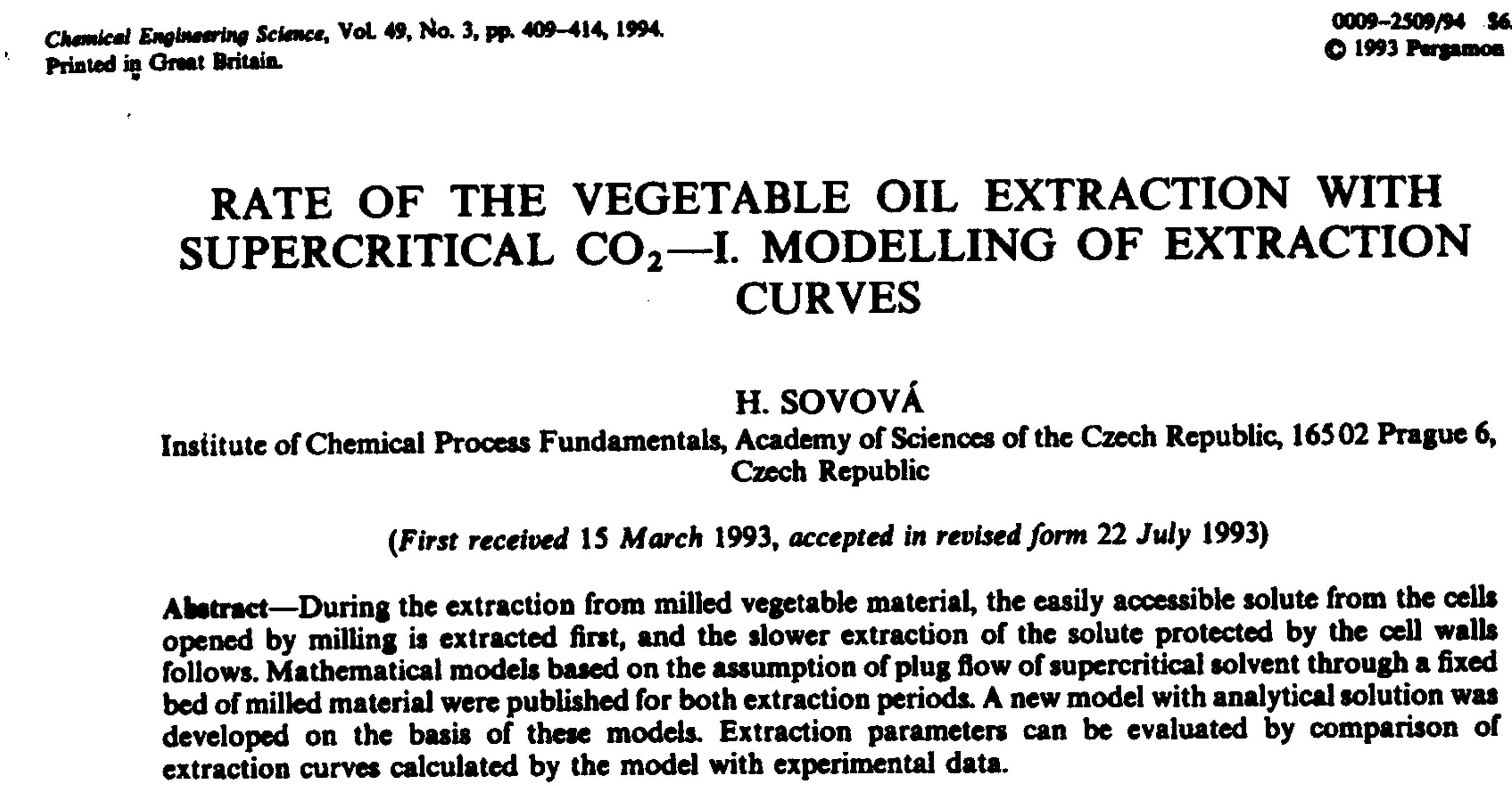
Preliminary Process of Extraction: Surface layers transferred to the solvent. Easy and fast

Secondary Process: Diffusion from pore surfaces and interior of the solid pores.

Diffusion controlled. At the end of extraction, a solution dispersed between the bulk solution and pore interiors.

- Bulk Solution remains outside
- Solution in pore interiors remain trapped.

SCF Extraction



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RATE OF THE VEGETABLE OIL EXTRACTION WITH SUPERCRITICAL CO_2—I. MODELLING OF EXTRACTION CURVES

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Abstract—During the extraction from milled vegetable material, the easily accessible solute from the cells opened by milling is extracted first, and the slower extraction of the solute protected by the cell walls follows. Mathematical models based on the assumption of plug flow of supercritical solvent through a fixed bed of milled material were published for both extraction periods. A new model with analytical solution was developed on the basis of these models. Extraction parameters can be evaluated by comparison of extraction curves calculated by the model with experimental data.

SCF Extraction

Extended Lack's Plug Flow Model

- SFE operation can be related to the time of extraction, by the evaluation of the extraction curve. The extraction curves are clearly divided into three sections:

1. Constant extraction rate (CER): the external surface of the particles is covered with solute (easily accessible solute) – the mass transfer resistance is the solvent phase.
2. Falling extraction rate (FER): failures in the external surface oil layer appear. The easily accessible solute is completely depleted at the extractor's entrance – the diffusion mechanism starts.
3. Diffusion-controlled: mass transfer occurs only by the diffusion in the bed and inside the solid substratum particles.

- To derive the Lack's plug flow model, Sovova proposed similar physical representation of the seed particles as being composed of cell broken up during grinding and of cells which are still intact.
- They hypothesized the existence of two mass transfer resistances during SFE. The first is located in the supercritical mixture and controls the extraction process until all the essential oil in the broken cells is exhausted. The second is in the walls of the undestroyed cells and controls the remaining part of the process.

SCF Extraction

These hypotheses were transferred to the mathematic model by introducing two mass balances for a bed element:

Solid phase: $$-p_s(1-\varepsilon)\frac{dX}{dt} = J(X,Y)$$

Liquid phase: $$p_F \cdot U\frac{\partial Y}{\partial h} = J(X,Y)$$

The X and Y are the solute mass ratio in the solid and fluid phases respectively, t is time, U is the superficial velocity, ps and pF are the solid and fluid phase densities respectively, ε is the total porosity (bed and particles), h is the axial direction, and J(X,Y) is the interfacial mass transfer rate. The boundary conditions are:

$X(h, t = 0) = X_0$, and
$Y(h=0, t)= 0$

SCF Extraction

- The easily accessible solute which surmounts only the diffusion resistance in the solvent is extracted first. When the solid-phase concentration decreases to Xk, mass transfer is retarded by the diffusion in the solid phase:

  $J(X > X_k, Y) > J(X \leq X_k, Y)$

- To solve Eqs. Mass balance equation earlier Sovova [1994] defined J(X,Y) as a function of the concentration difference using a local mass transfer coefficient for both phases. These definitions lead to an analytical solution of mass balance that divided the overall extraction curve into 3 regions: CER, FER and diffusion controlled period.
- By introducing the boundary conditions, despite the uniformity of solute in the solid phase, the Sovova's model, divide the total amount of solute (O) into two fraction: the easily accessible fraction or the most superficial one (P) and the difficult accessible fraction or inside un-ruptured cells one (K):

$$X_o = \frac{O}{N} \qquad X_p = \frac{P}{N} \qquad X_k = \frac{K}{N}$$

SCF Extraction

The solution for masss balance equation are:
CER period, t < tCER

$$m_{extr} = Y^{*}[1 - \exp(-Z)]Q_{CO_2} t \qquad \text{(Eq. 1)}$$

FER period, tCER ≤ t ≤ tFER

$$m_{extr} = Y^{*}[t - t_{CER} \exp(z_W - Z)]Q_{CO_2} \qquad \text{(Eq. 2)}$$

Diffusion controlled period, t ≥ tFER

$$m_{extr} = N\left\langle X_O - \frac{Y^{*}}{W} \ln\left\{1 + \left[\exp\left(\frac{WX_O}{Y^{*}}\right) - 1\right] \times \exp\left[\left(\frac{WQ_{CO_2}}{N}\right)(t_{CER} - t)\right]\frac{X_K}{X_O}\right\}\right\rangle$$

(Eq. 3)

SCF Extraction

The following restrictions are applied to Eqs. (1), (2) and (3):

Z, parameter of fast extraction period $$Z = \frac{N k_{Ya} p_{CO_2}}{Q_{CO_2}(1-\varepsilon) p_s}$$

t_{CER}, constant extraction rate period

$$t_{CER} = \frac{X_O - X_K}{Y^* Z}\frac{N}{Q_{CO_2}}$$

t_{FER}, falling extraction rate period

$$t_{FER} = t_{CER} + \frac{N}{Q_{CO_2} W}\ln\left[X_K + \frac{(X_O + X_K)\exp\left(W X_O / Y^*\right)}{X_O}\right]$$

W, mass transfer parameter in the solid phase

$$W = \left(\frac{N k_{Xa}}{Q_{CO_2}(1-\varepsilon)}\right) = k\frac{Z Y^*}{X_K}$$

z_W, dimensionless coordinate

$$z_W = \frac{Y^* Z}{W X_O}\ln\left\{\frac{X_O \exp\left[\left(W Q_{CO_2} / N\right)\left(t - t_{CER}\right)\right] - X_K}{X_O - X_K}\right\}$$

SCF Extraction

Analytical assumptions

- To estimate the parameters for the model the following procedure was adopted:
- The initial solute mass ratio (X_O) was set equal to the total amount of oil extracted by both SFE followed by Soxhlet Standard extraction.
- The time t_{CER} was initially calculated as the interception between the first and the second lines of the spline.
- Mass ratio difference was calculated as proposed by *Ferreira et al. [1999] shown in (Eq. 4).
- The mass transfer coefficient, k_{Ya} of the solvent phase of the solvent phase for the CER period was estimated by (Eq. 6).
- The parameter W that includes the solid phase mass transfer coefficient was estimated using eq. show in previous slide.

*http://www.sciencedirect.com/science/article/pii/S0260877401002126

SCF Extraction

$\Delta \bar{Y}$, mass ratio difference

$$\Delta \bar{Y} = \frac{(Y^* - Y_{in}) - (Y^* - Y_{CER})}{\ln\left[(Y^* - Y_{in})/(Y^* - Y_{CER})\right]} \qquad \text{(Eq. 4)}$$

$\Delta \bar{X}$, overall mass ratio of solute

$$\Delta \bar{X} = \frac{(X_P + X_K)}{2} \qquad \text{(Eq. 5)}$$

k_{Ya}, mass transfer coefficient of the solvent phase

$$k_{Ya} = \frac{M_{CER}}{p_{CO_2} S H_b \Delta \bar{Y}} \qquad \text{(Eq. 6)}$$

k_{Xa}, mass transfer coefficient of the solid phase

$$k_{Xa} = \frac{k_{Ya} p_{CO_2} \Delta \bar{Y}}{p_s \Delta \bar{X}} \qquad \text{(Eq. 7)}$$

SCF Extraction

Raw data for SFE of black pepper essential oil

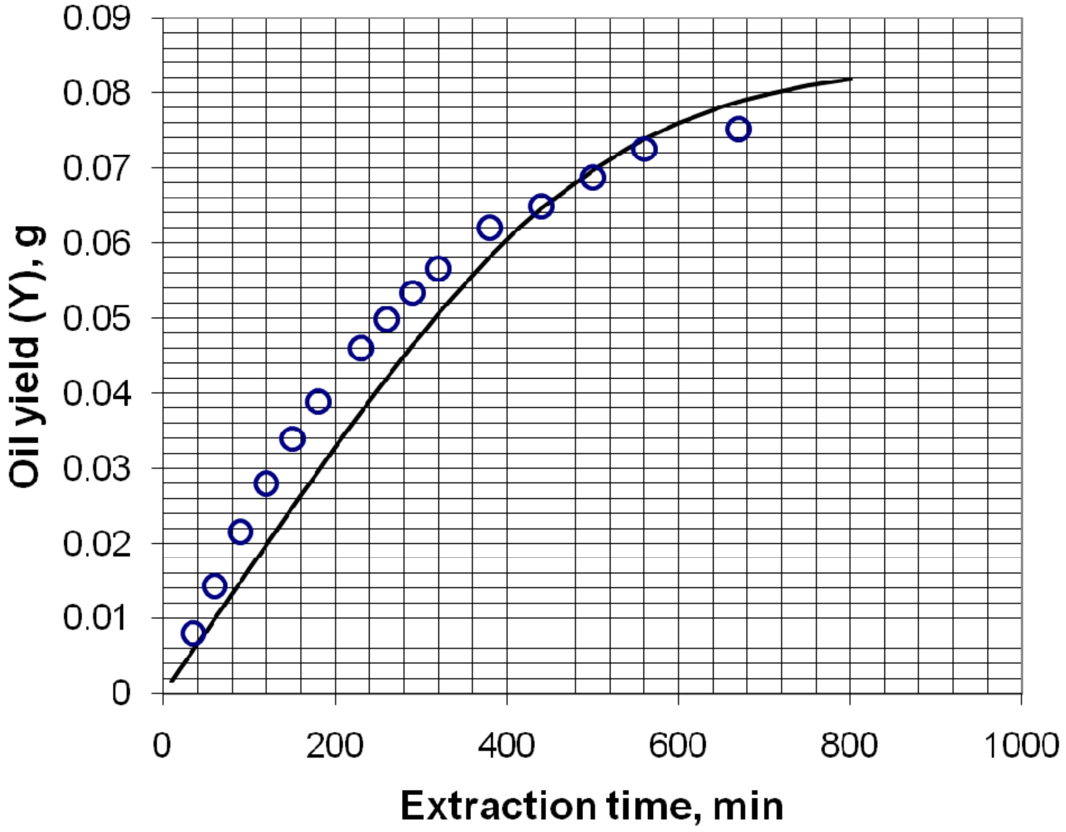
Duration, min	CO2 Consumed, ml	Oil Collected, g	Total CO2 Consumed, g	Total oil extracted, g	Oil Yield, g/g
35	36.23	0.2386	30.4441	0.2386	0.0080
60	29.93	0.1889	55.5942	0.4275	0.0143
90	29.93	0.2204	80.7444	0.6479	0.0217
120	30	0.1914	105.9534	0.8393	0.0281
150	30.84	0.1771	131.8683	1.0164	0.0340
180	29.16	0.1481	156.3714	1.1645	0.0389
230	50.17	0.2131	198.5293	1.3776	0.0460
260	30.1	0.1154	223.8223	1.4930	0.0499
290	29.96	0.1051	248.9977	1.5981	0.0534
320	29.93	0.0961	274.1479	1.6942	0.0566
380	60.03	0.1636	324.5911	1.8578	0.0621
440	61.13	0.0845	375.9586	1.9423	0.0649
500	59.97	0.1141	426.3514	2.0564	0.0687
560	60.19	0.1147	476.9291	2.1711	0.0726
670	102.64	0.0772	563.1775	2.2483	0.0751
				2.5225	

SCF Extraction

Before proceed to the simulation of Lack's plug flow model, some parameters have to be computed for further calculation.

Total oil collected = 2.5225g
Total oil collected at CER = 1.1645g (estimation)
Oil of unfree region = 1.358g
Mass of cellulosic structure = 27.4796g
Solvent flow rate = 0.8406g/min
Total CO2 consumed = 563.177463g
Length of bed, Hb = 10.5cm
Extractor sectional area, S = 10.073892cm2

SCF Extraction



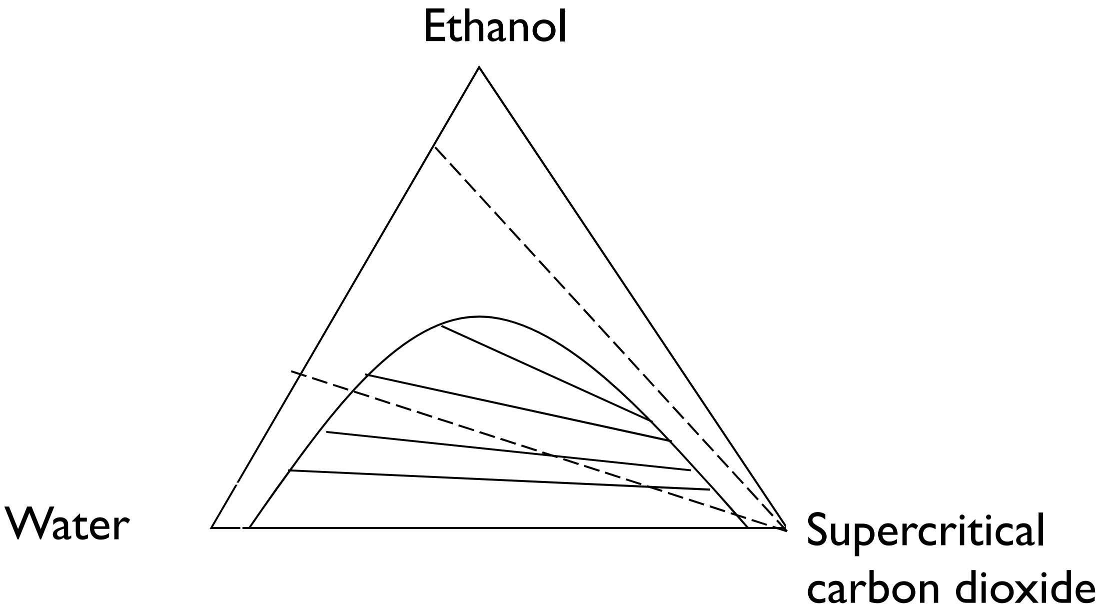
Open circle – experiment

Straight line –Plug flow model

SCF Extraction

Liquid-SF Extraction

Ethanol enrichment by supercritical CO_2 is probably not the best extracting fluid for ethanol enrichment!



http://www.cbu.edu/~rprice/lectures/extract.html

SCF Extraction

Phase equilibrium date for tie line construction

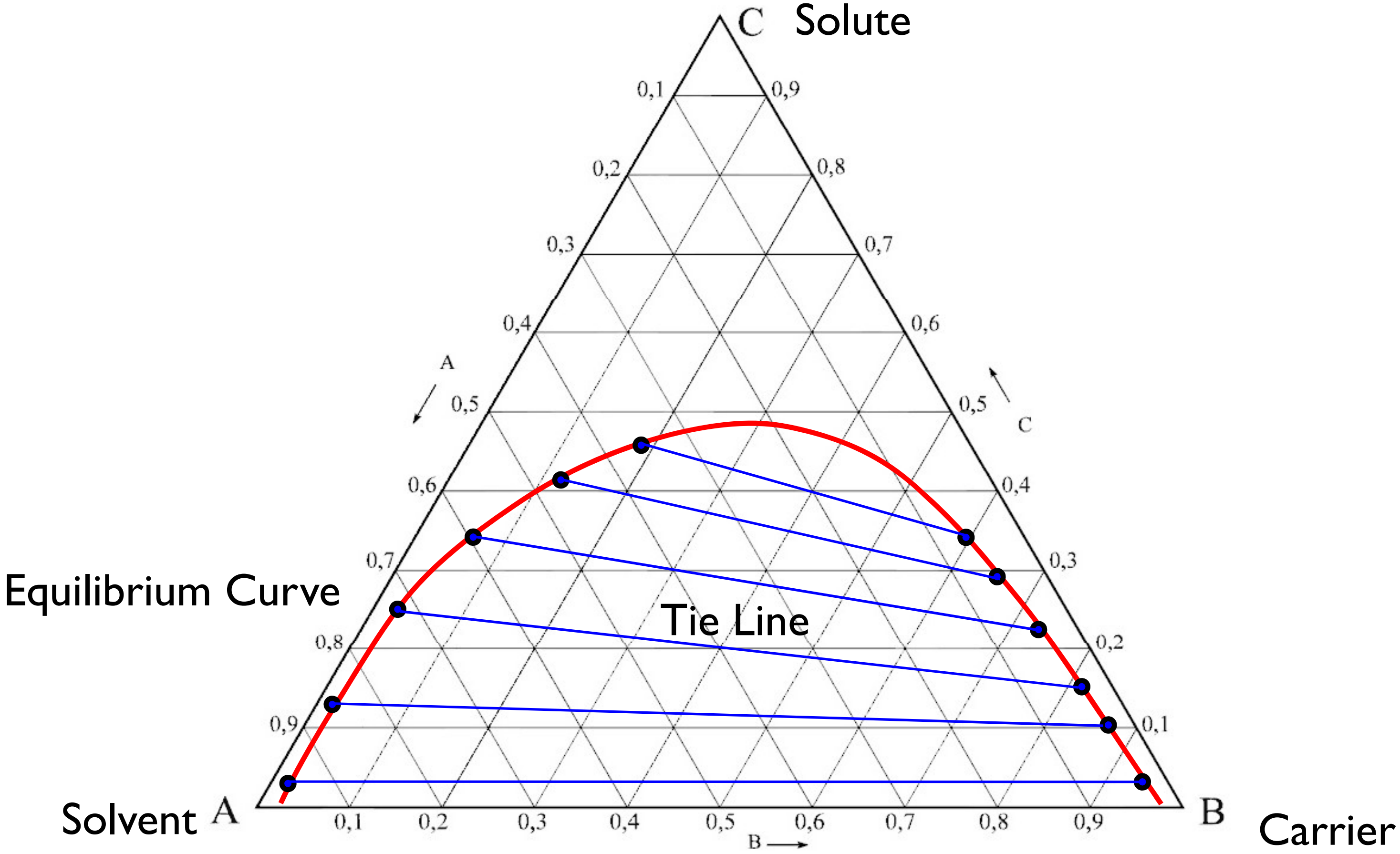
Extract phase			Raffinate phase		
SC CO2	**Isopropyl alcohol**	**water**	**SC CO2**	**Isopropyl alcohol**	**water**
80.7	**17.8**	**2.9**	**0.1**	**1.6**	**96.9**
59	**35.9**	**5.1**	**0.1**	**4.9**	**95**
35.9	**53.8**	**10.3**	**0.2**	**10.4**	**89.4**
25	**58.3**	**16.7**	**0.3**	**15.1**	**84.6**
14.6	**56.9**	**28.5**	**0.8**	**21.9**	**77.3**
10	**52.5**	**37.5**	**1.5**	**27.4**	**71.1**

Paulaitis, Kander and Diandreth 1984

Solvent – SC CO2
Solute – Isopropyl alcohol
Carrier - Water

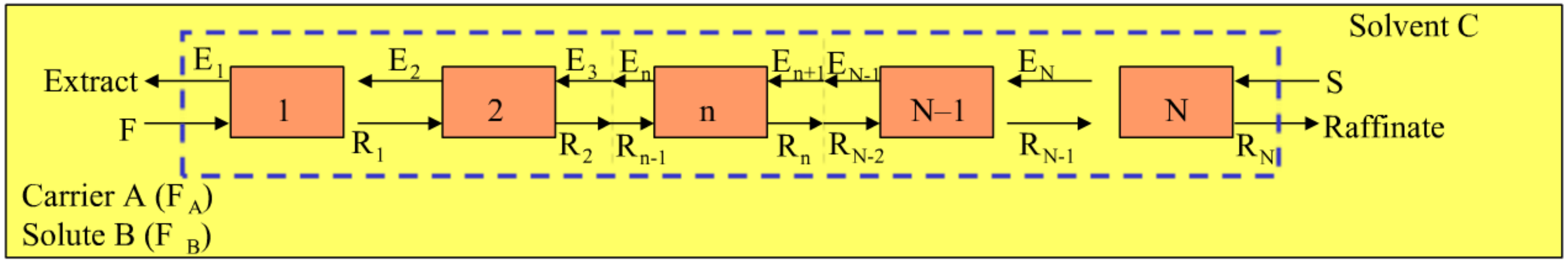
SCF Extraction

Hunter-Nash liquid-liquid extraction



SCF Extraction

Conceptual demonstration of theoretical stages involved

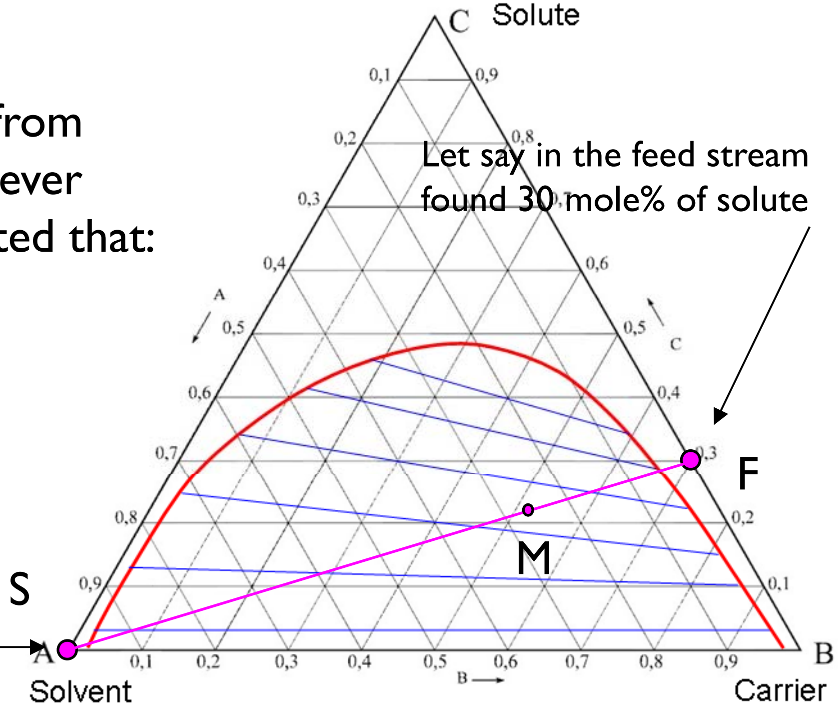


Step 1) Find the mixing point M = F + S

Step 2) Determine mixing point composition from component material balances or applying the lever arm principle. In which lever arm principle stated that:

$$S(\overline{SM}) = F(\overline{FM})$$

Now we measure the total length of SF line is 60 cm and S/F = (FM)/(SM) = 1/2, hence, (FM) = 20 cm and (SM) = 40 cm.

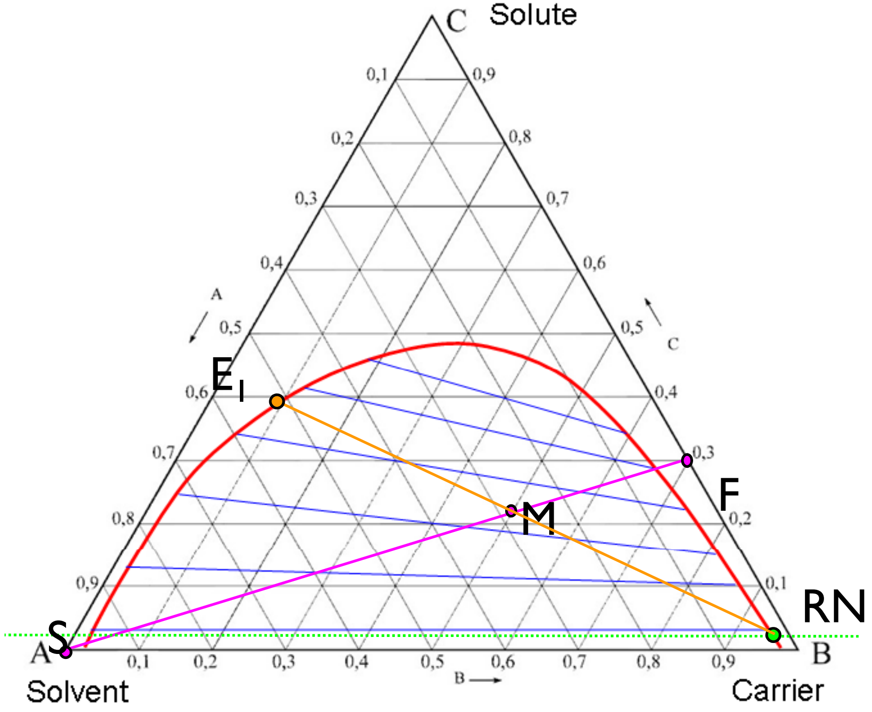


Let say in the feed stream found 30 mole% of solute

Let assume we used solvent with no solute at all.

SCF Extraction

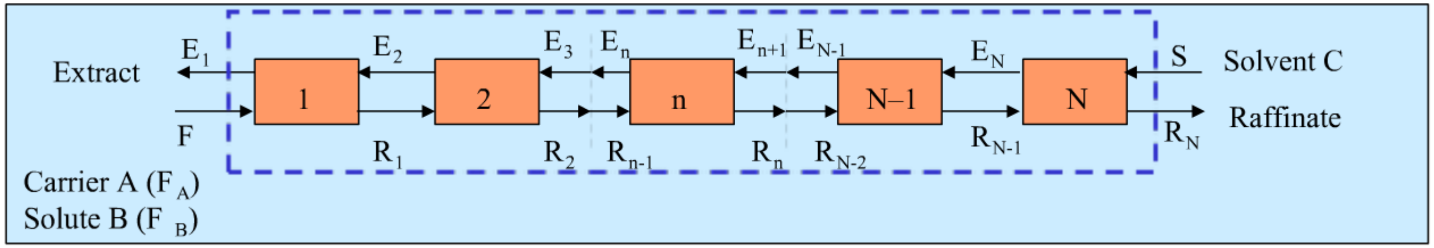
Step 3) Since we know RN lies on the equilibrium curve and we know the composition of solute in rafinate $(x_a)_{RN}$, we can determine $(x_b)_{RN}$ and $(x_c)_{RN}$
Step 4) Since we know RN, M and E1 all lie on a mixing line we can locate E1 by extending a line from RN through M to the equilibrium curve where it intersects E1.



We left 3% of solute after extraction

SCF Extraction

Construction of operating line



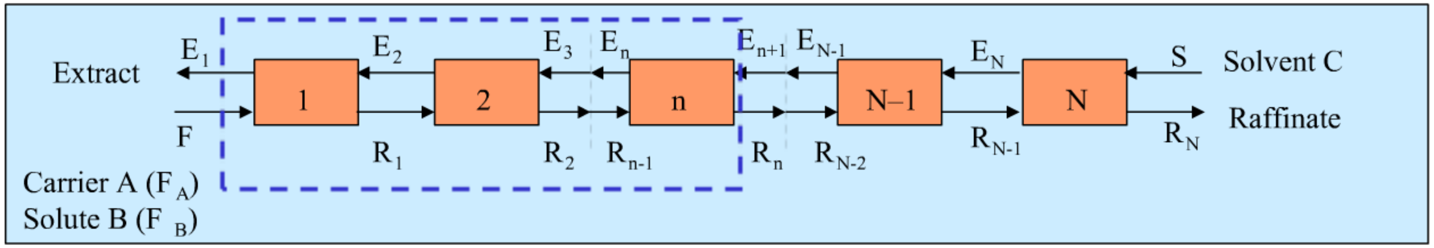
Operating Points and Lines

Mass Balance around entire cascade:

$$F + S = R_N + E_1$$

We define the operating point P as the difference between passing streams:

$$F - E_1 = R_N - S \equiv P$$



Mass Balance around the first n stages:

$$F + E_{n+1} = R_n + E_1$$

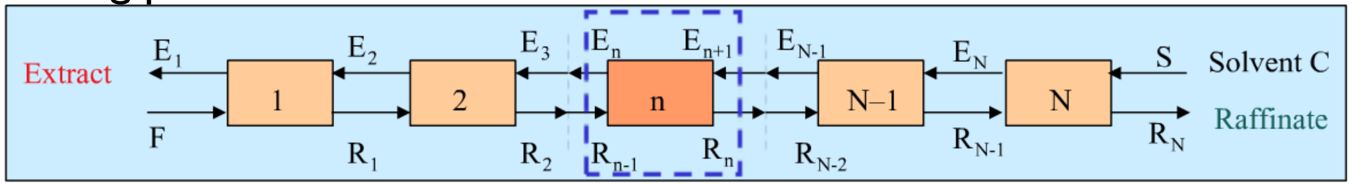
We rearrange this equation to find that all passing streams are related by the same operating point P.

$$F - E_1 = R_n - E_{n+1} = P$$

http://www.powershow.com/view/17b21c-MmU1Y/Hunter_Nash_LiquidLiquid_Extraction_flash_ppt_presentation

SCF Extraction

Operating point



Operating Points and Lines

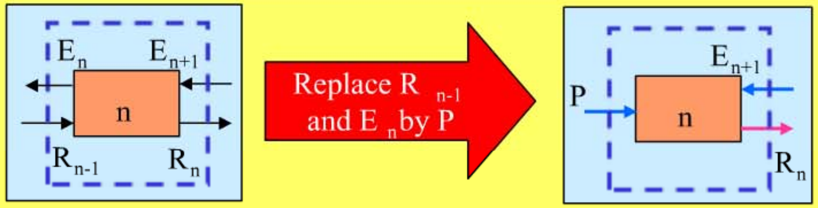
Mass Balance around an internal stage:

$$R_n + E_n = R_{n-1} + E_{n+1}$$

We can rearrange the above expression to find that R_n is just a mixing point between P and E_{n+1}.

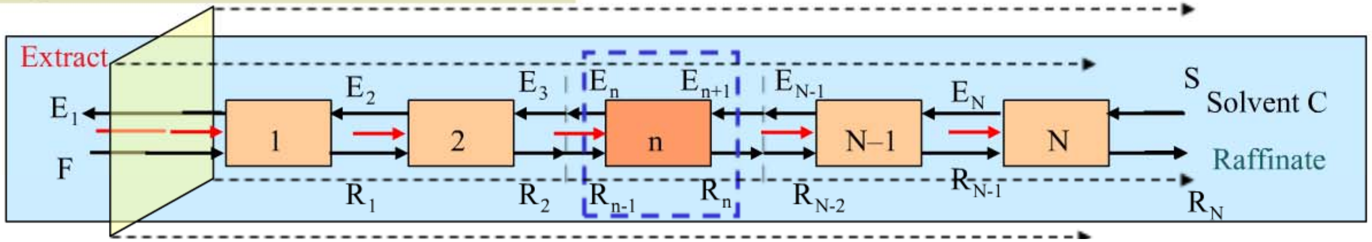
$$R_n = R_{n-1} - E_n + E_{n+1} = P + E_{n+1}$$

The following figure illustrates this concept: The stream R_n is the mixing point between P and E_{n+1} because P is the net flow into stage n from passing streams R_{n-1}, and E_n.



The N mass balances around the N individual stages result in:

$$F - E_1 = R_{n-1} - E_n = R_N - S = P$$



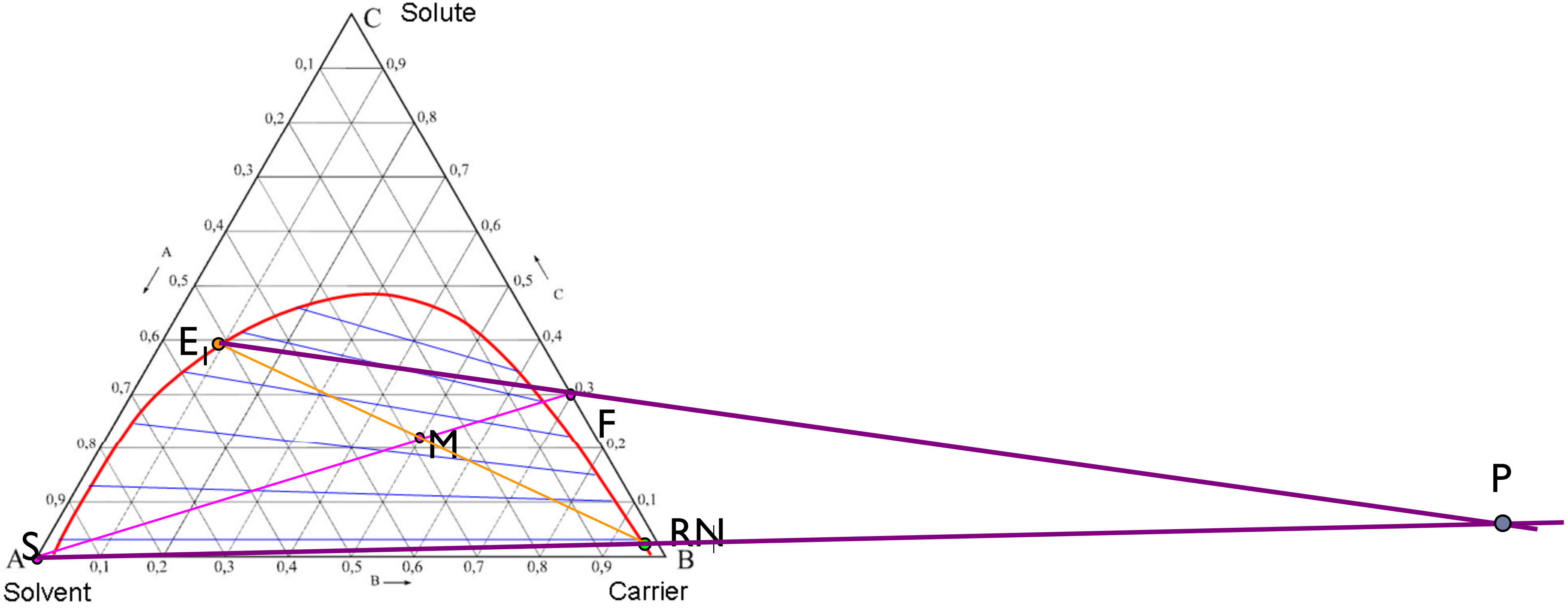
SCF Extraction

Step 5) Locate the operating point by finding the intersection of operating lines for the leftmost and rightmost stages

a) draw a line through E1 and F.

b) draw a line through S and R.

c) Locate the intersection P. This point is the operating point P.



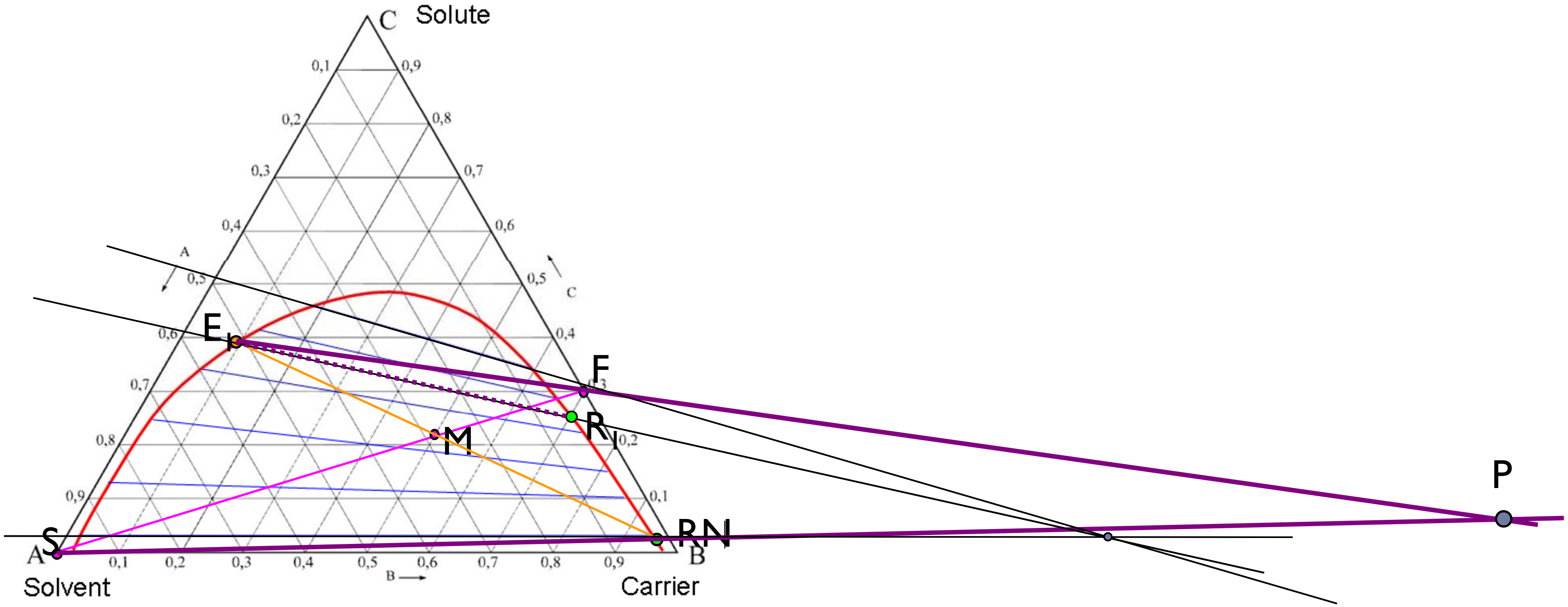
SCF Extraction

Step 6) Locate point R1 from the tie line intersecting E1

Step 7) Draw a line from the operating point P through R1 to the extract side of the equilibrium cruve. The intersection locates E2.

Step 8) Locate point R2 from a tie line.

Step 4) Repeat steps 2 and 3 until RN is obtained.



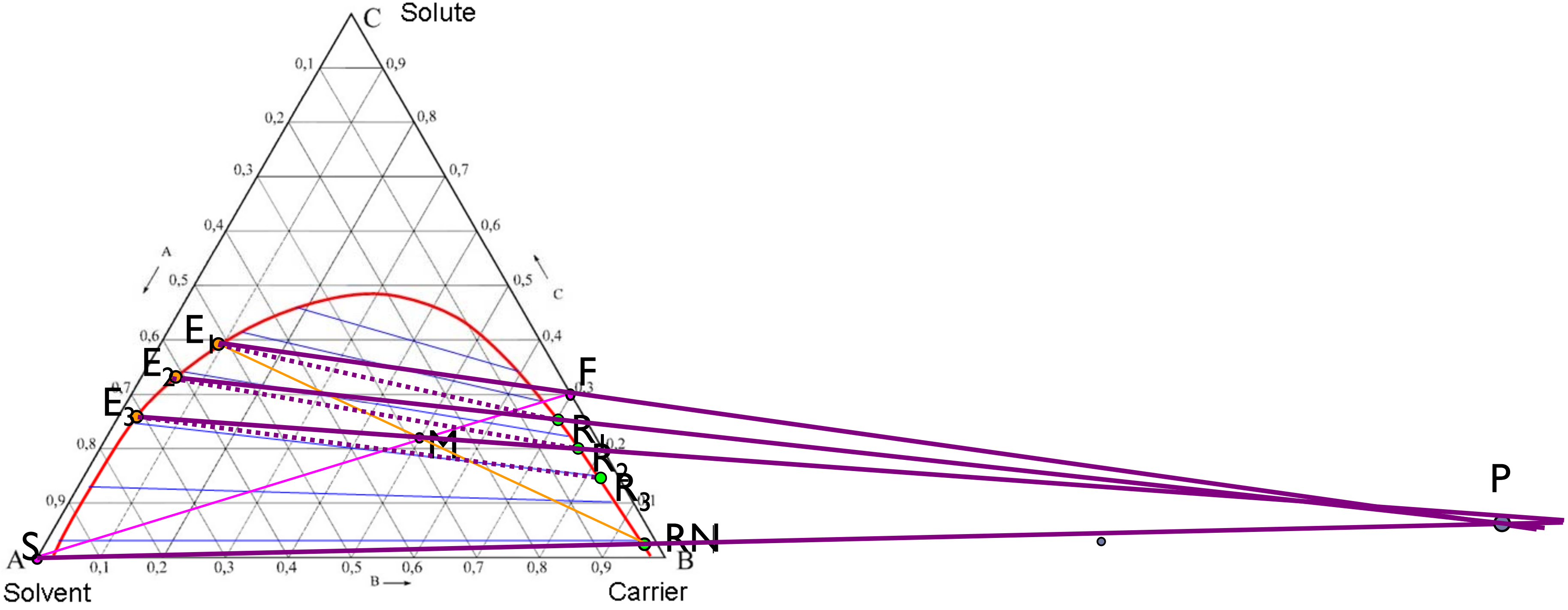
SCF Extraction

Step 6) Locate point R1 from the tie line intersecting E1

Step 7) Draw a line from the operating point P through R1 to the extract side of the equilibrium cruve. The intersection locates E2.

Step 8) Locate point R2 from a tie line.

Step 4) Repeat steps 2 and 3 until RN is obtained.



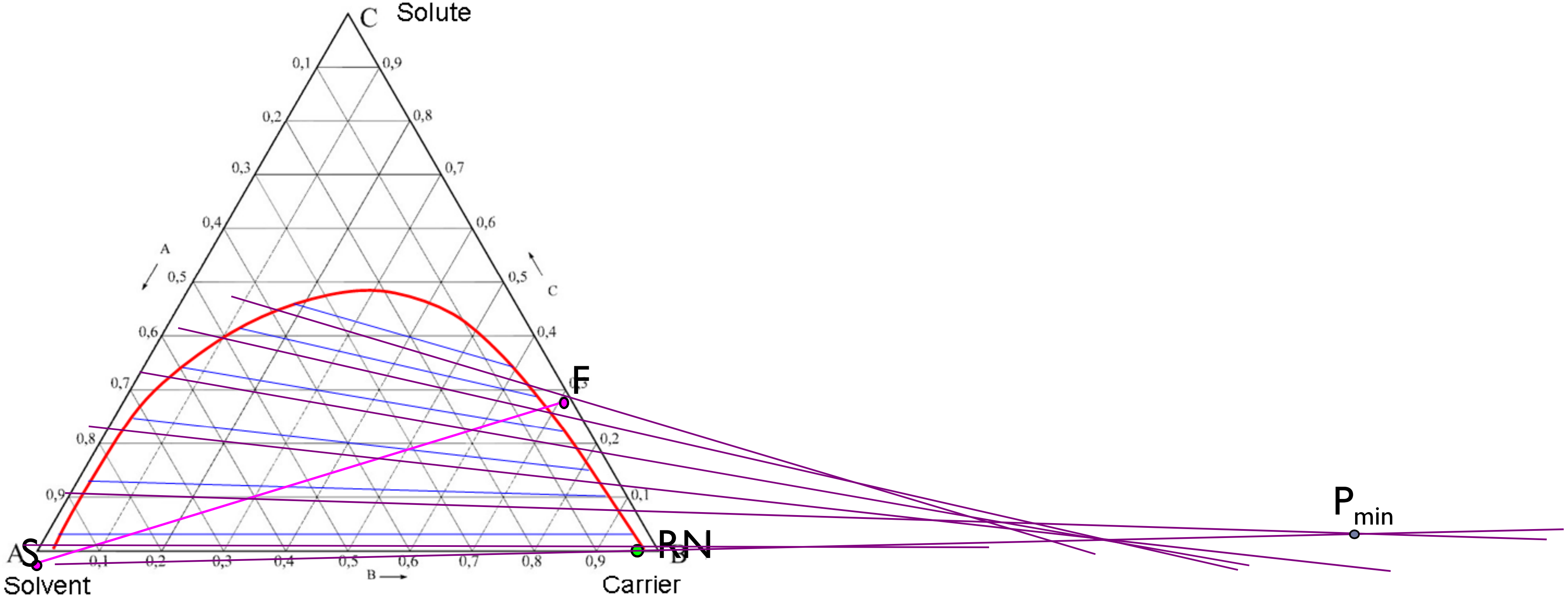
SCF Extraction

To locate minimum solvent

Step 1) Locate the raffinate operating line by extending a line from S through R_N

Step 2) Extend the tie lines to intersect the operating line

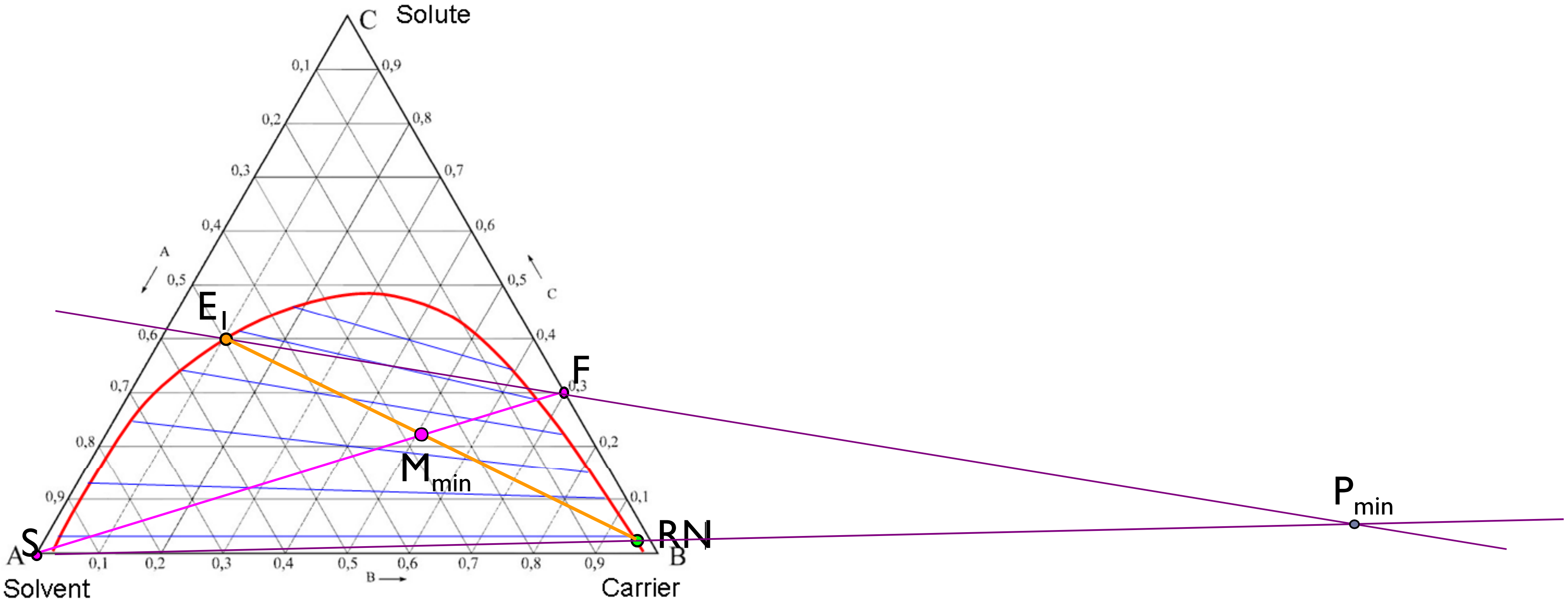
Step 3) The tie line that intersects furthers from R_N gives the minimum operating point P_{min}.



SCF Extraction

Step 4) Extend a line from P_{min} through F to the extract side of the equilibrium curve to find E_I.

Step 5) Extend a line from E_I to R_N. The intersection with the line SF gives the minimum mixing point.



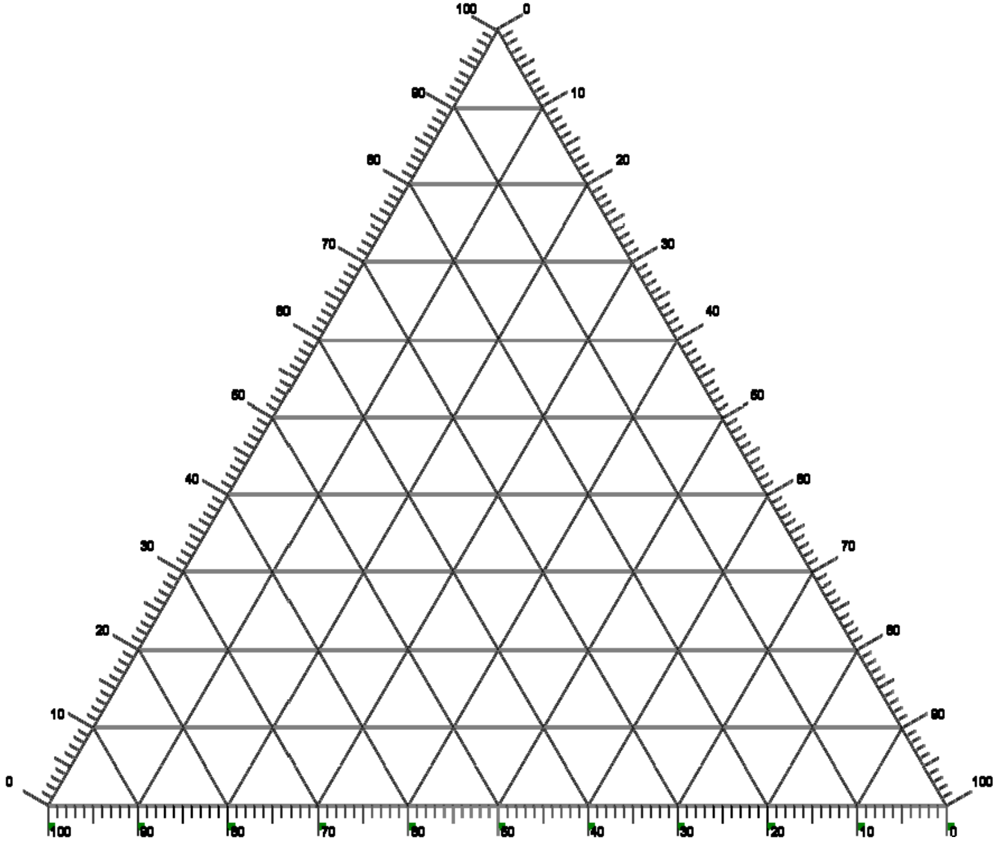
Discussion

- Subject: Extraction of acetone (A) from water (C) by 1,1,2-trichloroethane (S)
- Given: 1,000 kg/h of 45 wt% A in C. Liquid-liquid equilibrium data. 10 wt% A in raffinate.
- Find: Using Hunter-Nash method with an equilateral triangle diagram.
- (a) Minimum flow rate of S.
- (b) Number of equilibrium stages for solvent rate of 1.5 times minimum.
- (c) Flow rate and composition of each stream leaving each stage.

	Acetone, Weight Fraction	Water, Weight Fraction	Trichloroethane, Weight Fraction
Extract	0.60	0.13	0.27
	0.50	0.04	0.46
	0.40	0.03	0.57
	0.30	0.02	0.68
	0.20	0.015	0.785
	0.10	0.01	0.89
Raffinate	0.55	0.35	0.10
	0.50	0.43	0.07
	0.40	0.57	0.03
	0.30	0.68	0.02
	0.20	0.79	0.01
	0.10	0.895	0.005

The tie-line data are:

Raffinate, Weight Fraction Acetone	Extract, Weight Fraction Acetone
0.44	0.56
0.29	0.40
0.12	0.18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