DESIGNING LIQUID-LIQUID EXTRACTION COLUMNS

An Introduction

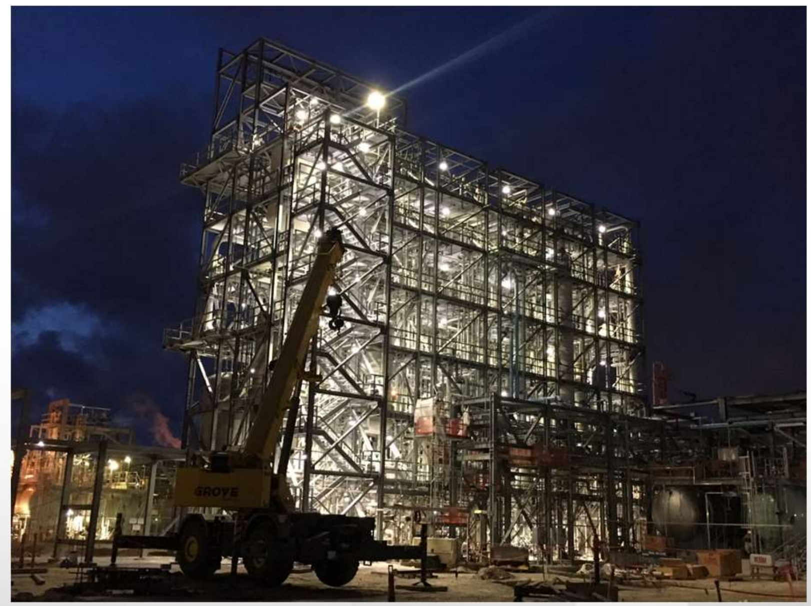
AIChE - East Tennessee Local Section

December 8th, 2020

Koch Modular
PROCESS SYSTEMS

Koch Modular at a Glance

Koch Modular is a Joint Venture company, partnered with KOCH-GLITSCH, one of the world's most prominent suppliers of mass transfer equipment. Koch-Glitsch's parent company is Koch Industries, one of the largest privately held corporations in the United States.



Technical Expertise

For over **25 years** Koch Modular has successfully designed and supplied complete modular constructed process systems for the worldwide Chemical Processing Industry.

Our customers rely upon us for our technical expertise and quality systems.

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Koch Modular Presenter Biographies

Don Glatz is the Manager of Extraction Technology at Koch Modular. Don's activities include the evaluation and optimization of extraction processes plus scale-up and design of extraction systems. He has been working in this field for the past 25 years and has published a number of papers and articles covering this subject. Don holds a BS in chemical engineering from Rensselaer Polytechnic Institute and an MBA from Fairleigh Dickinson University.

Brendan Cross is a Senior Process Engineer at Koch Modular that works in the Extraction Technology Group. Brendan is responsible for liquid-liquid extraction application evaluation, extraction column and pilot test design, and commissioning and process startup. He has been with Koch Modular for over 10 years and also has experience in distillation and process development. Brendan holds a BS in chemical engineering Columbia University.

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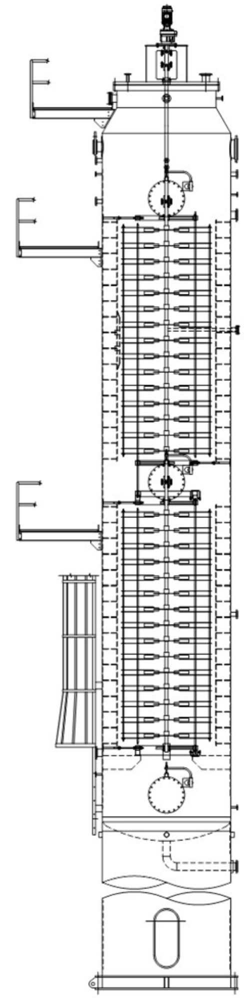
Typical Applications

When is it prudent to use extraction?

When you want to:

- Remove high boiling organics from dilute aqueous streams such as waste water or fermentation broths
- Recovery of non-volatile components which are typically inorganic chemicals
- Extract water soluble components from immiscible organic streams – quite often referred to as a “water wash”
- Separate multiple component mixtures often utilizing fractional extraction technique
- Separate heat sensitive products
- Process azeotropic and close boiling mixtures
- Avoid a high cost distillation solution



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Industries Using Extraction Technology

Chemical	▪ Recovery of acetic acid from dilute solutions ▪ Washing of acids/bases, polar compounds from organics ▪ Recovery of valuable chemicals from aqueous solutions
Metals/Mining	▪ Copper production ▪ Recovery of rare earth elements
Polymer Processing	▪ Recovery of caprolactam for nylon manufacture ▪ Separation of catalyst from reaction products ▪ Water extraction of water soluble components
Biochemical Processing	▪ Recovery of carboxylic acid from fermentation broths ▪ Recovery of valuable "oil" from algae broths
Effluent Treatment	▪ Removal and recovery of phenol, DMF, DMAC ▪ Removal of nitrated organics ▪ Wastewater processing
Inorganic Chemicals	▪ Purification of phosphoric acid

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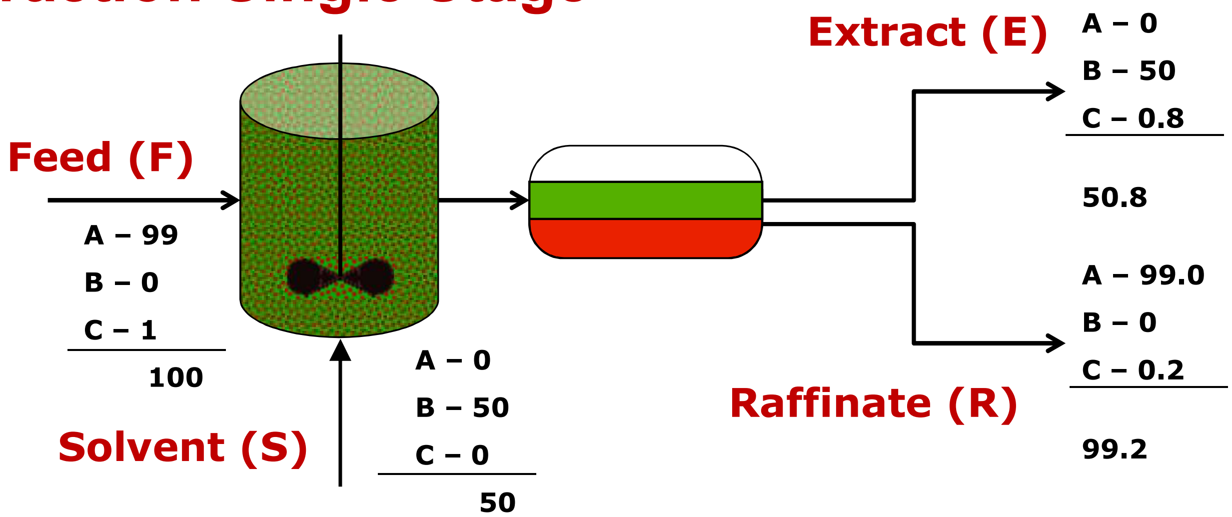
Simple Extraction Single Stage



Fraction Unextracted ➔ $U = \frac{\text{Solute in Raffinate}}{\text{Solute in Feed}} = \frac{0.2}{1.0} = 0.2$

Distribution Coefficient ➔ $M = \frac{\text{Conc. Solute in Extract}}{\text{Conc. Solute in Raffinate}} = \frac{0.8/50}{0.2/99} = 7.92$

Extraction Factor ➔ $E = \left(S/F\right)(M) = \left(50/99\right)(7.92) = 4.0$

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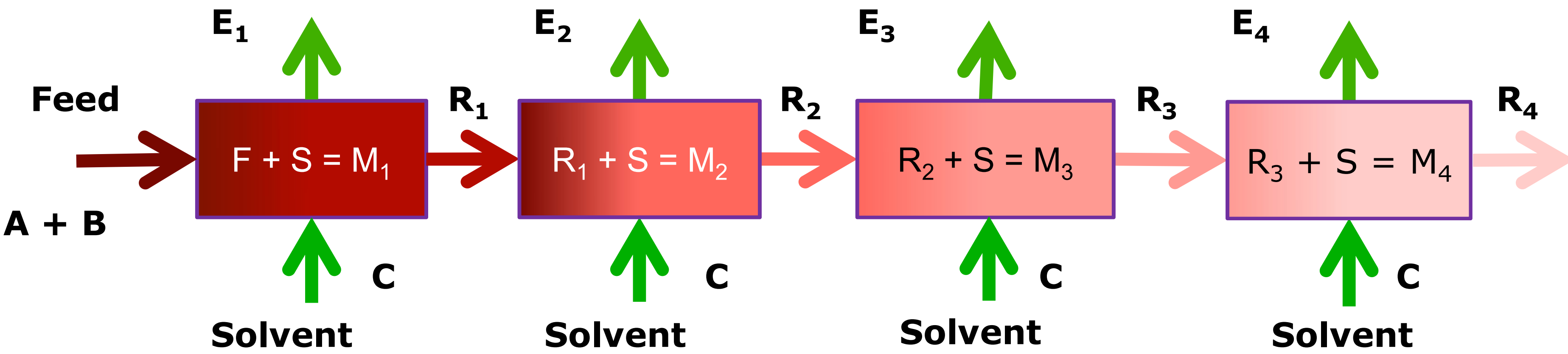
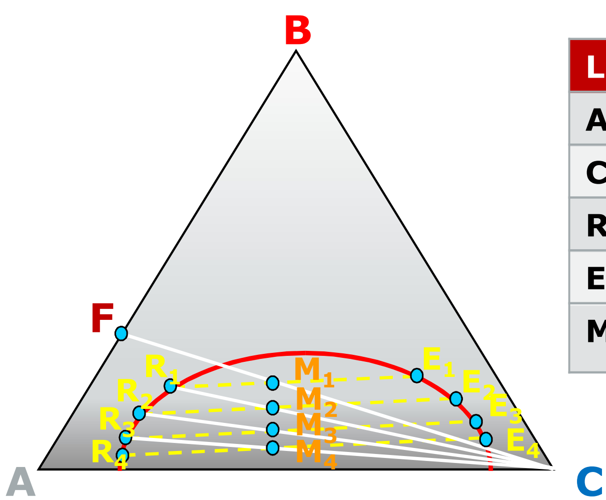
Cross Flow Extraction





LEGEND	
A, B	Components in feed
C	Component in solvent
R_x	Raffinate from stage x
E_x	Extract (made up of components B & C)
M_x	Composition of two phase mixture

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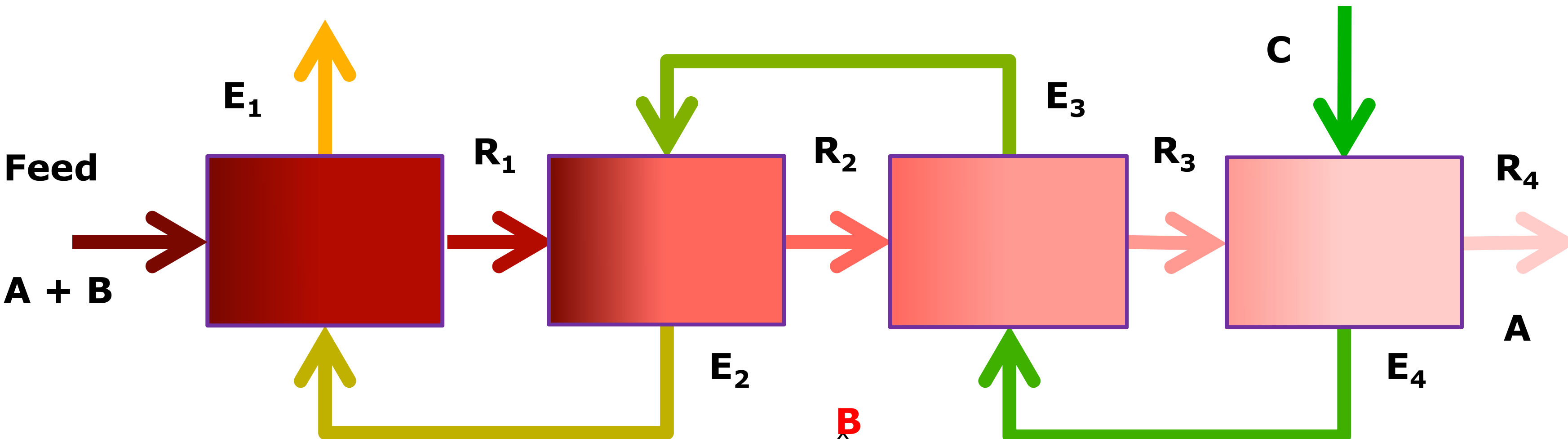
Countercurrent Flow Extraction



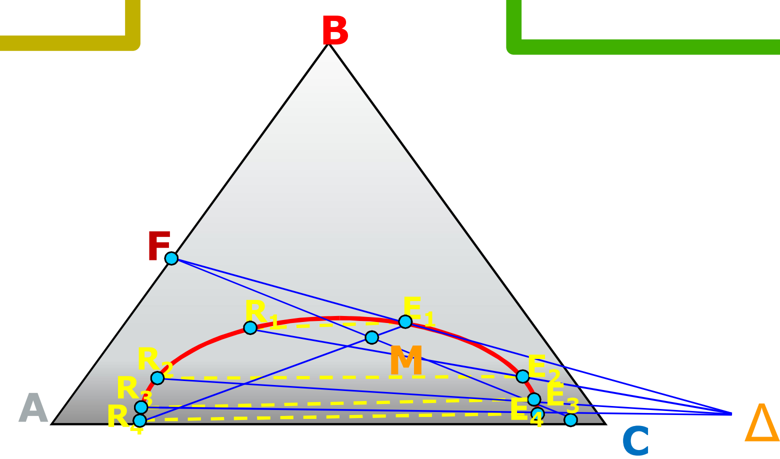
Equations

$F + S = M$

$E_1 + R_4 = M$

$F + S = E_1 + R_4$

$F - E_1 = R_4 - S = \Delta$



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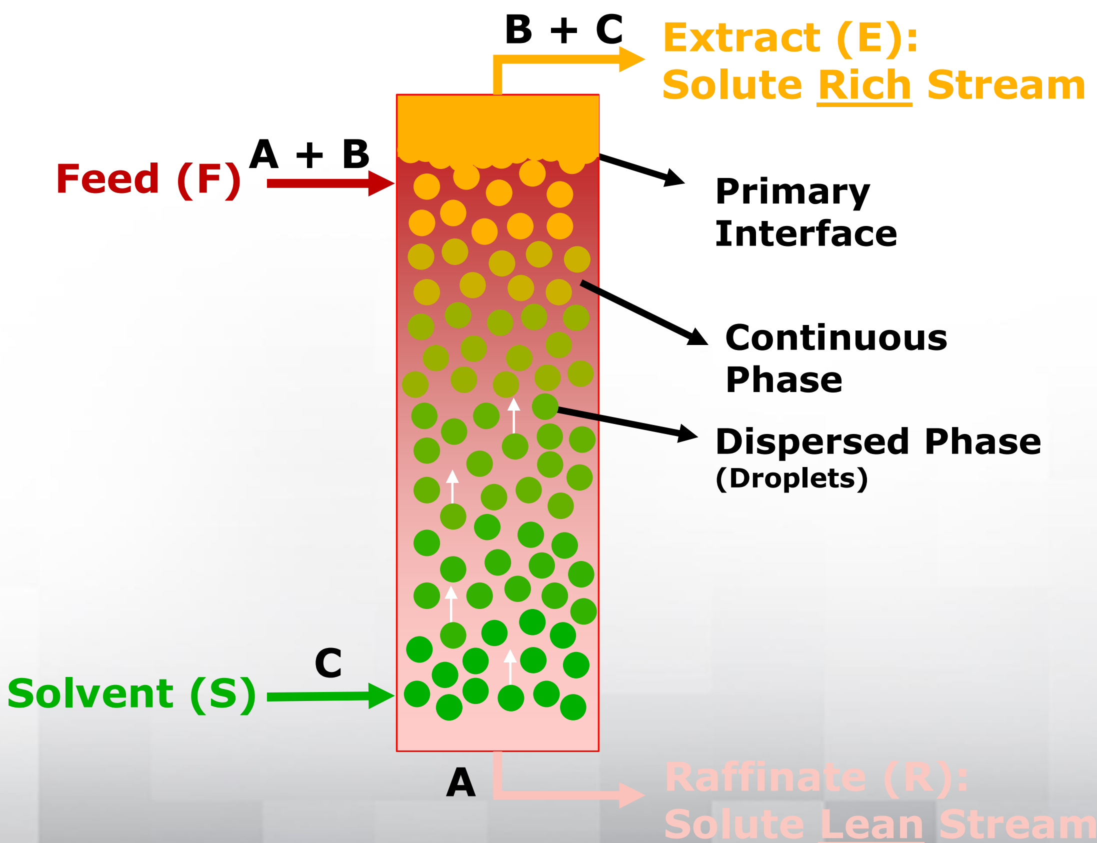
Countercurrent Extraction



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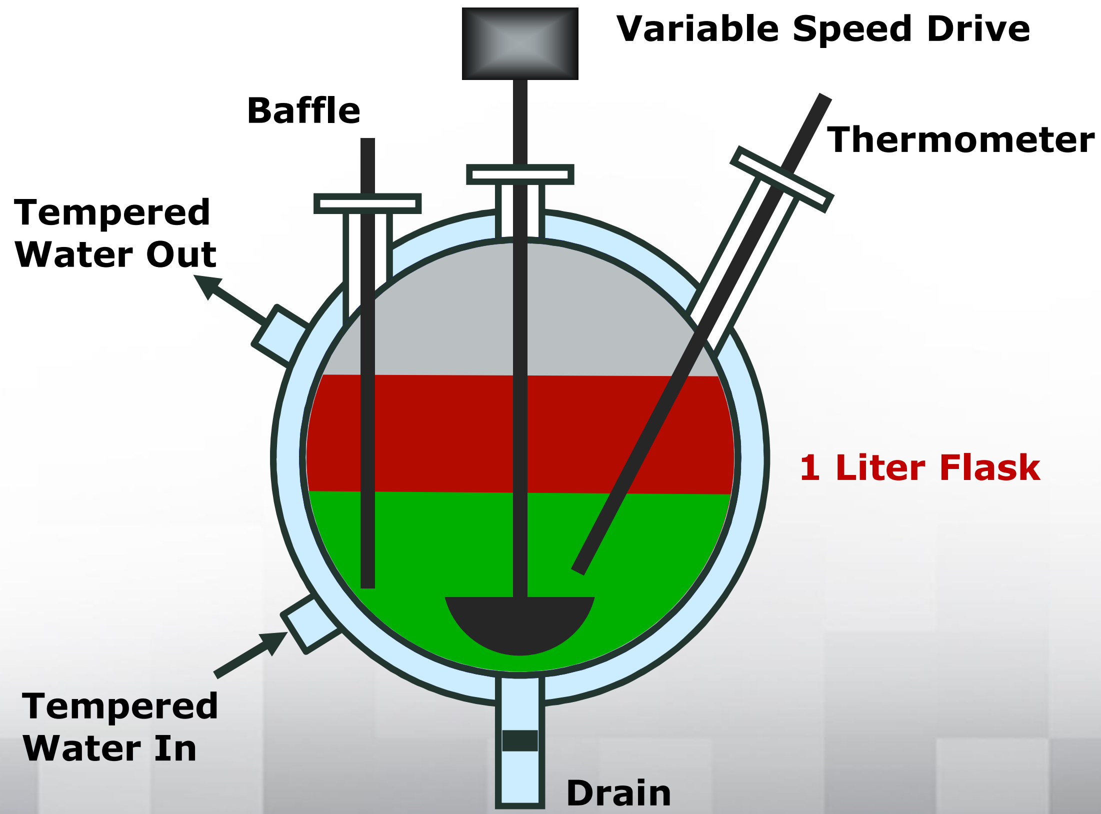
Bench Scale Test Apparatus (Liquid-Liquid Equilibrium Development)



Used to:

- Generate distribution coefficients
- Screen solvents
- Perform qualitative observations

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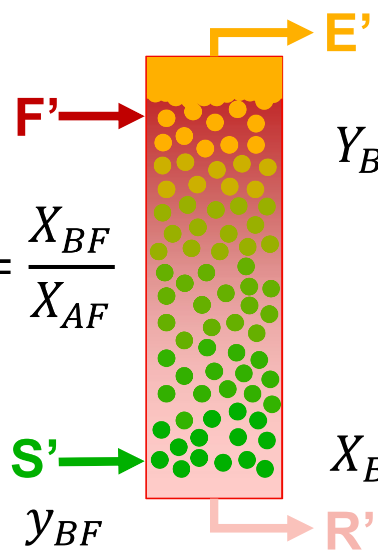
LLE Equilibrium and Operating Lines

Solute Free Basis



$$X_{BF} = \frac{X_{BF}}{X_{AF}}$$

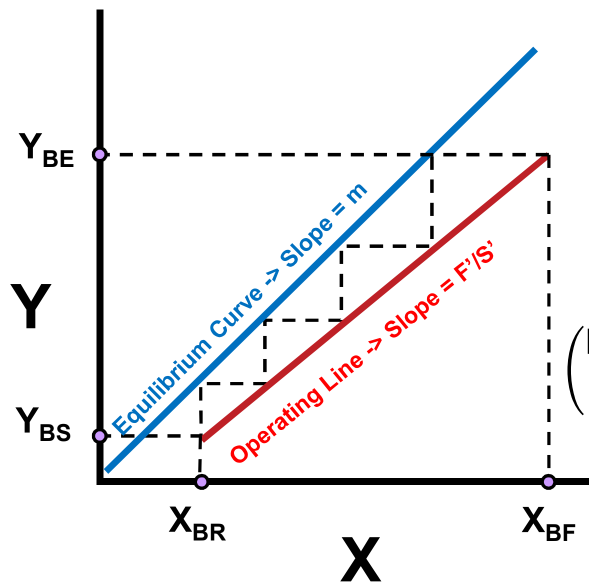
$$Y_{BE} = \frac{y_{BE}}{y_{AR} + y_{CE}}$$

$$X_{BR} = \frac{x_{BR}}{x_{AR} + x_{CR}}$$

$$Y_{BS} = \frac{y_{BF}}{y_{AS} + y_{CS}}$$

$$F' = F(x_{AR})$$
$$S' = S(y_{AS} y_{CS})$$
$$E' = E(y_{AE} y_{CE})$$
$$R' = R(x_{AR} x_{CR})$$

Graphical Solution



$$m = \frac{Y_{B^*}}{X_{B^*}}$$

(Distributon Coefficient on Solute Free Basis)

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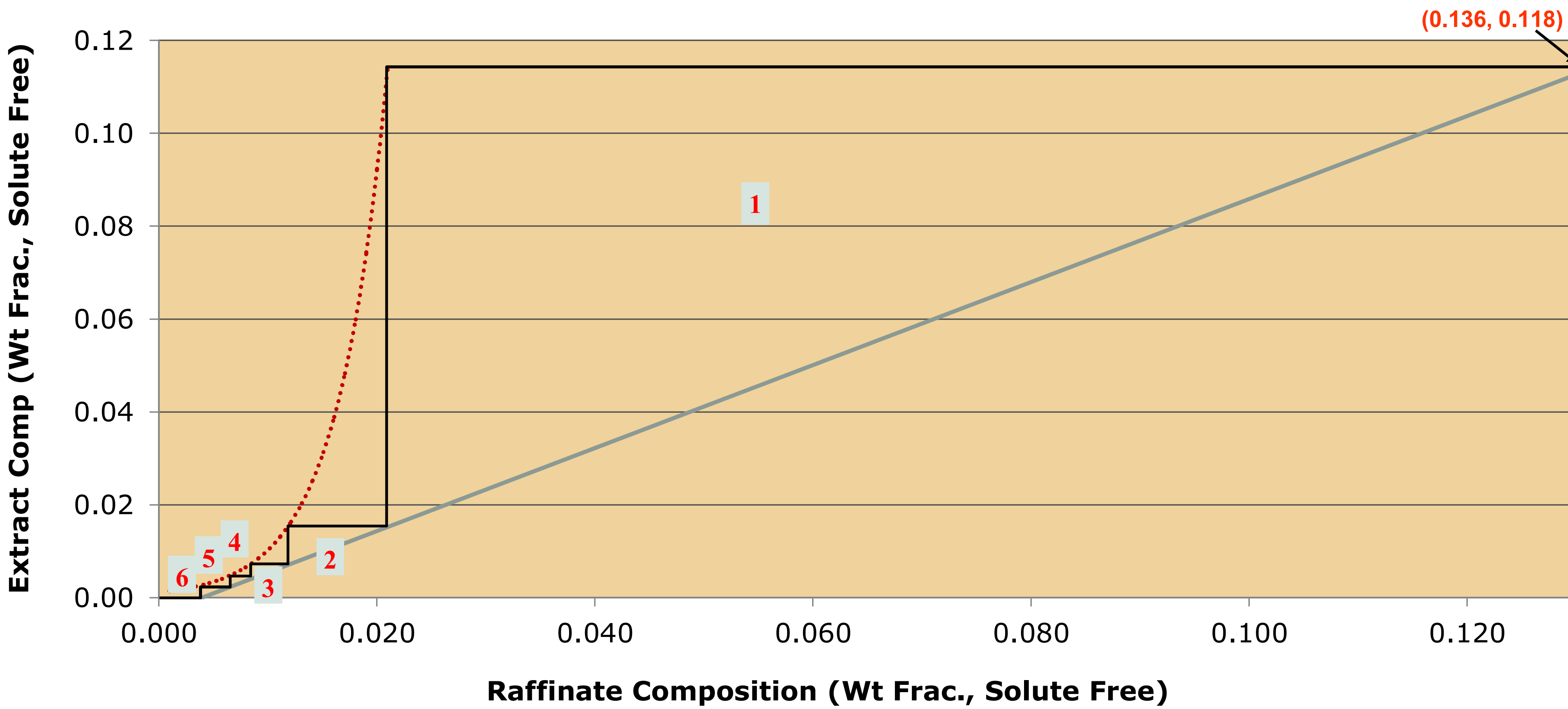
Graphical Determination of Theoretical Stages

98% Solute Extraction, S/F = 1.0 mass basis



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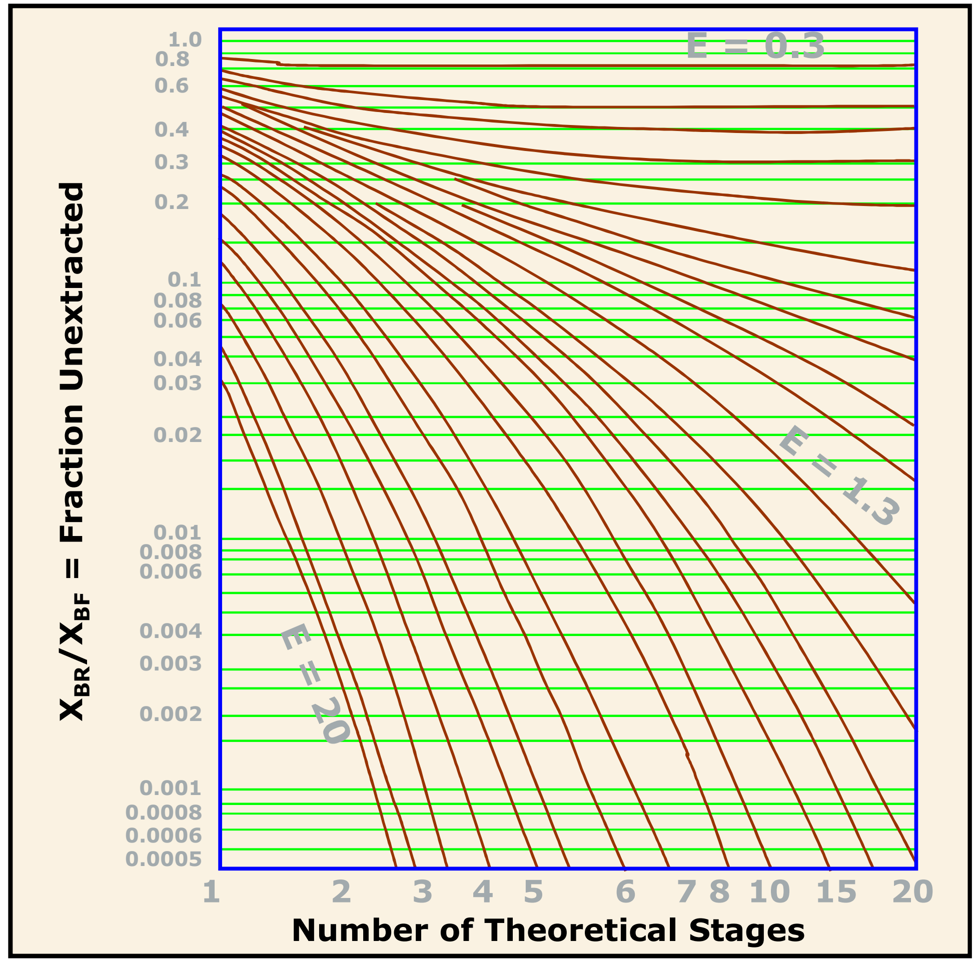
Kremser Equation

$$n = \frac{\mathrm{LOG}\left[\left(\dfrac{x_f - {y_s}/{m}}{x_n - {y_s}/{m}}\right)\left(1-\dfrac{1}{E}\right)+\dfrac{1}{E}\right]}{\mathrm{LOG}\,E}$$



n	=	Number of theoretical stages required
x_f	=	Conc. of solute in feed on solute free basis
x_n	=	Conc. of solute in raffinate on solute free basis
y_s	=	Conc. of solute in solvent on solute free basis
m	=	Distribution coefficient
E	=	Extraction factor = (m)(S/F)

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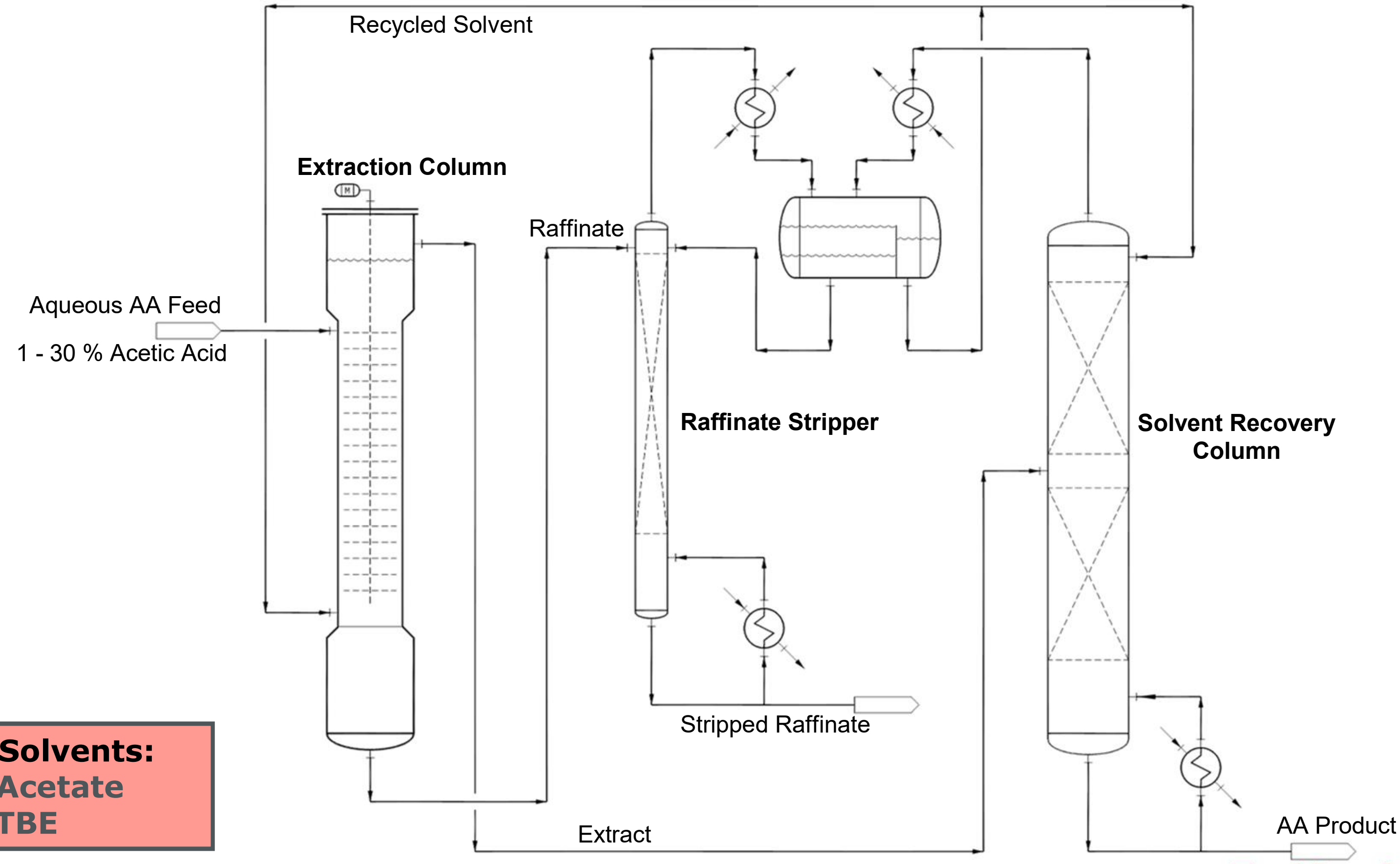
Recovery of Acetic Acid from Water Using a Low Boiling Solvent



Typical Solvents:
Ethyl Acetate
MTBE

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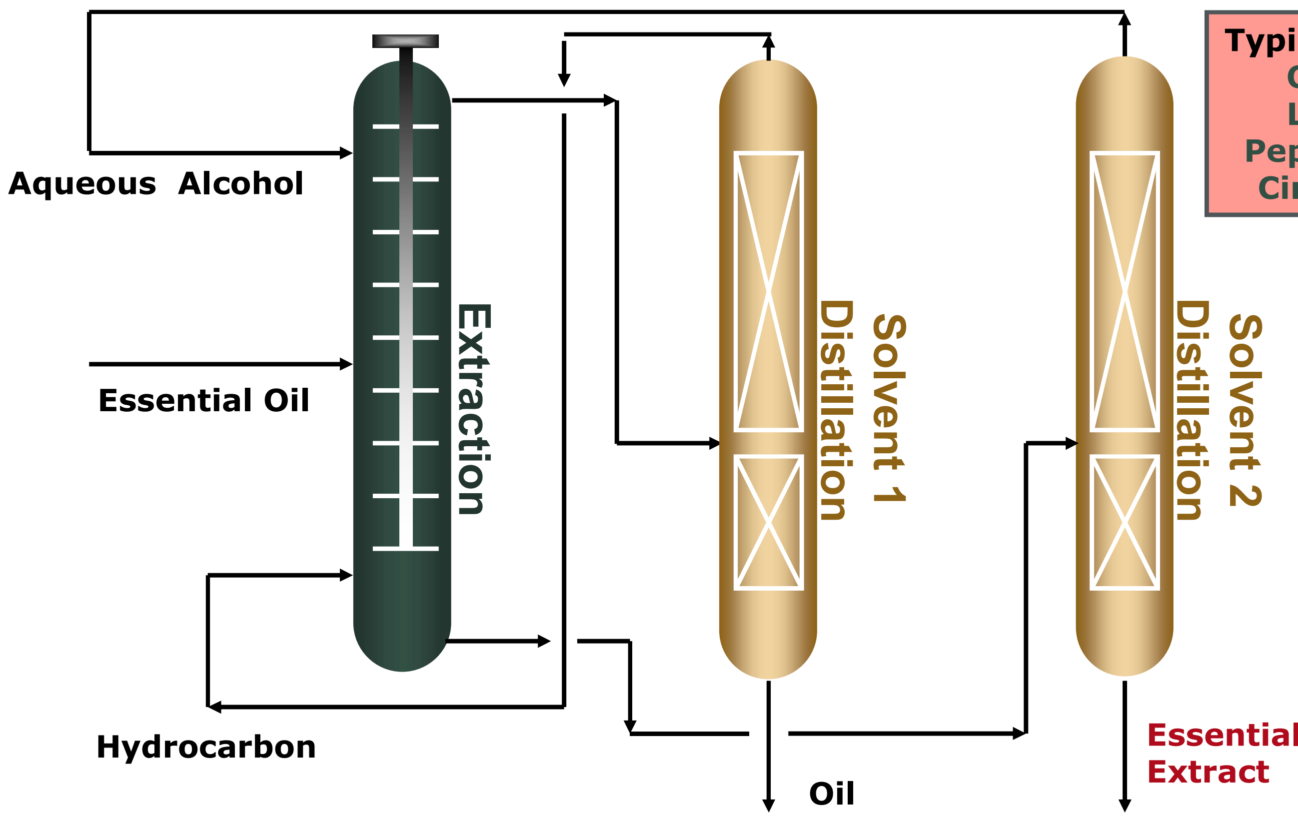
Fractional Extraction of Flavors and Aromas



Typical Products:
Orange Oil
Lemon Oil
Peppermint Oil
Cinnamon Oil

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Major Types of Extraction Equipment

Mixer Settlers

Used primarily in the metals industry due to:

- Large flows
- Intense mixing
- Long Residence time
- Corrosive fluids
- History

Column Contactors

Static

Spray

Rarely used

Packed

Used in:

- Refining
- Petrochemicals

Example:

- Random
- Structured
- SMVP™

Tray

Used in:

- Refining
- Petrochemicals

Example:

- Sieve
- **Baffle Tray**

Agitated

Pulsed

Used in:

- Nuclear
- Inorganics
- Chemicals

Example:

- Packed
- Tray
- Disc & Donut

Rotary

Example:

- RDC
- **SCHEIBEL®**

Reciprocating

Example:

- **KARR®**

Used in:

- Chemicals
- Petrochemicals
- Refining
- Pharmaceutical

Centrifugal

Used primarily in the pharmaceutical industry due to:

- Low Volume
- Short Residence time
- Handles Small Gravity Diff.
- History

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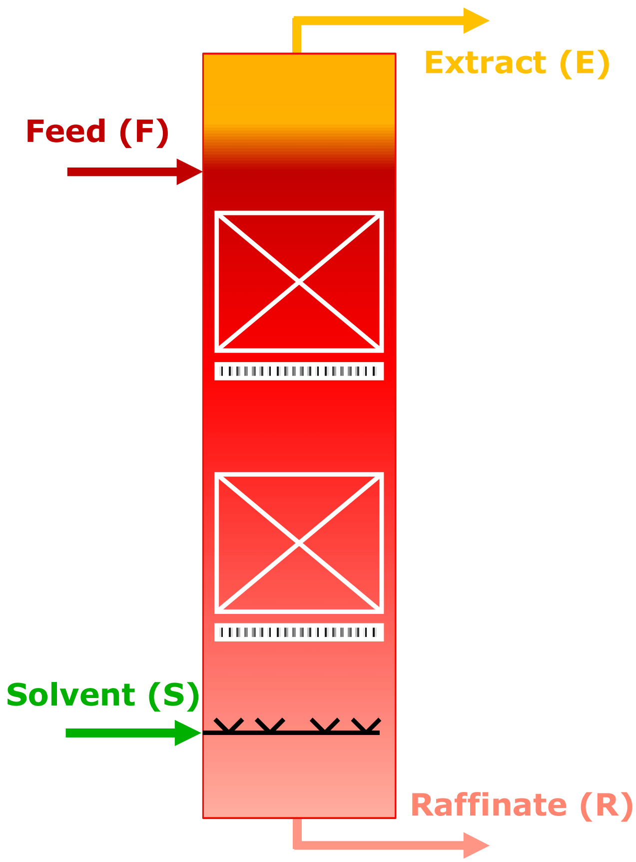
Packed Column



Characteristics

- High capacity:
  - 500-750 gal/ft2-hr (Random)
  - 20-30 M3/M2-hr (Random)
  - 1,000-2,000 gal/ft2-hr (Structured)
  - 40-80 M3/M2-hr (Structured)
- Limited as to which phase can be dispersed – internals MOC selection is critical
- Affected by changes in wetting characteristics
- Poor efficiency due to backmixing and wetting
- Not good for fouling service
- Limited turndown flexibility
- Requires low interfacial tension for economic usefulness

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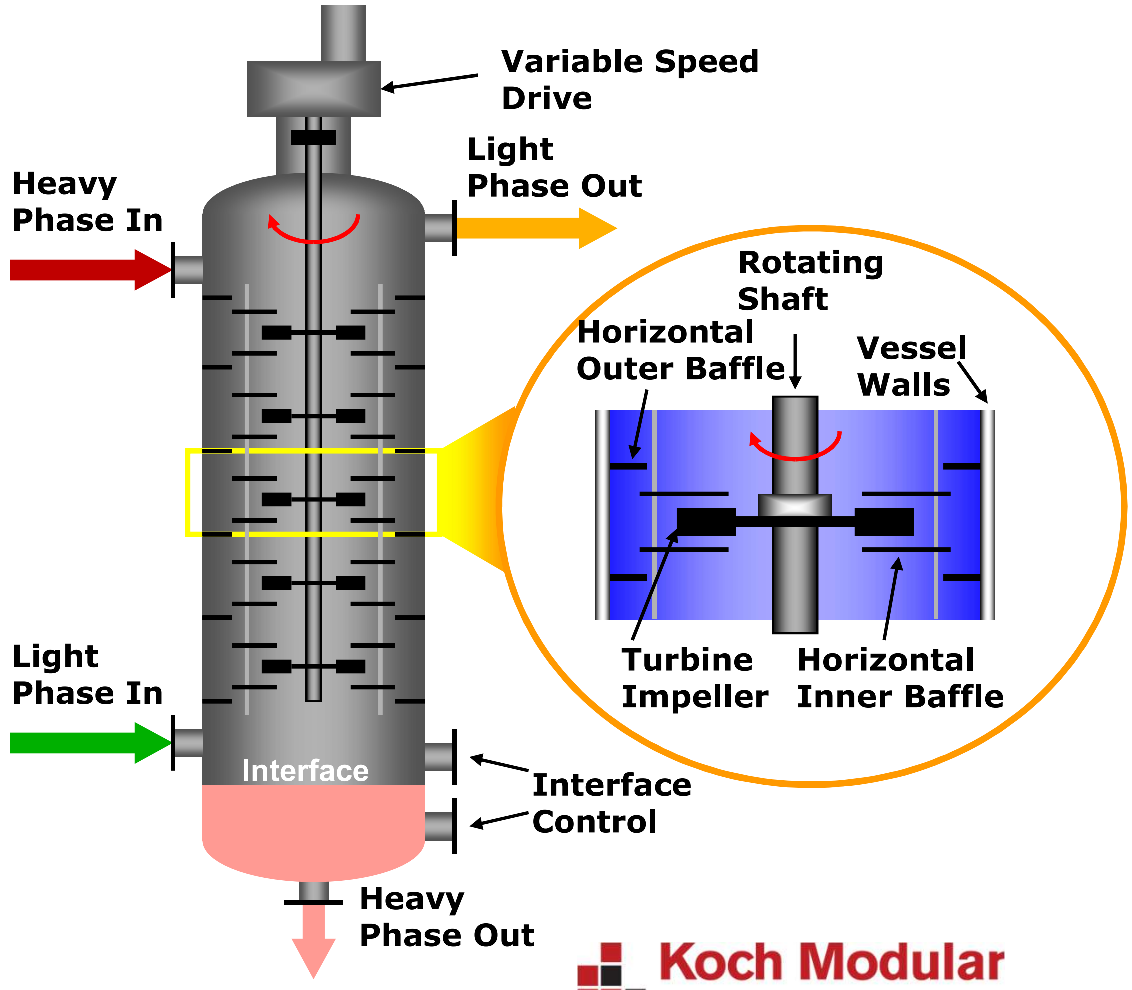
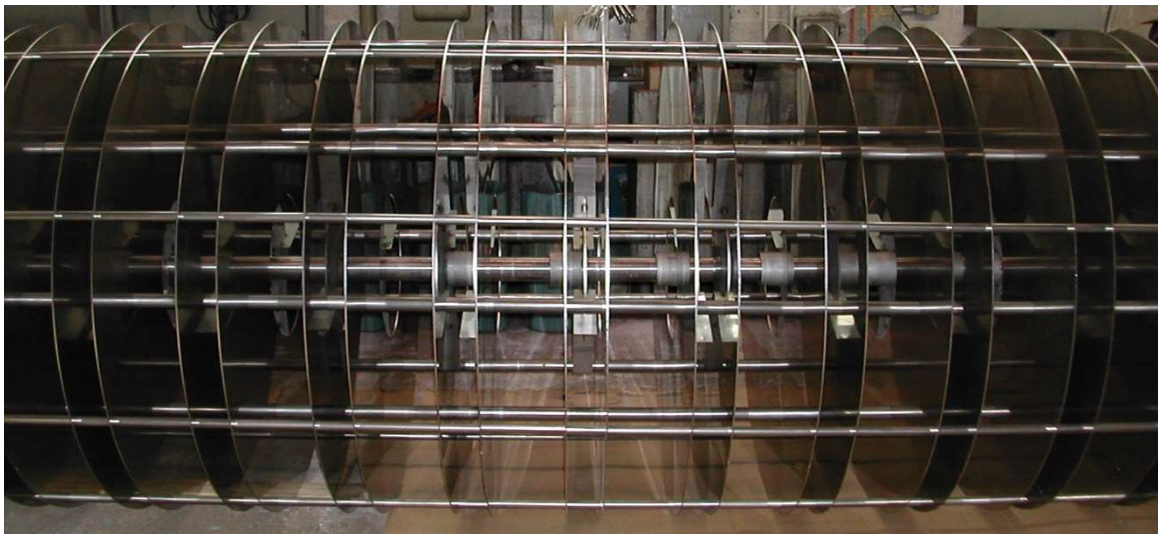
SCHEIBEL® Column

Characteristics

- Reasonable capacity:
  - 350-600 gal/ft^2-hr
  - 15-25 M^3/M^2-hr
- High efficiency due to turbine impellers and internal baffling
- Best suited when many stages are required
- Good turndown capability (4:1) and high flexibility
- Not recommended for highly fouling systems or systems that tend to emulsify
- Typical commercial operating speed: 15-75 RPM



SCHEIBEL® Column Internals



Internals for a 6.5 foot (2 meter) diameter SCHEIBEL® Column

SCHEIBEL® Column internals installation

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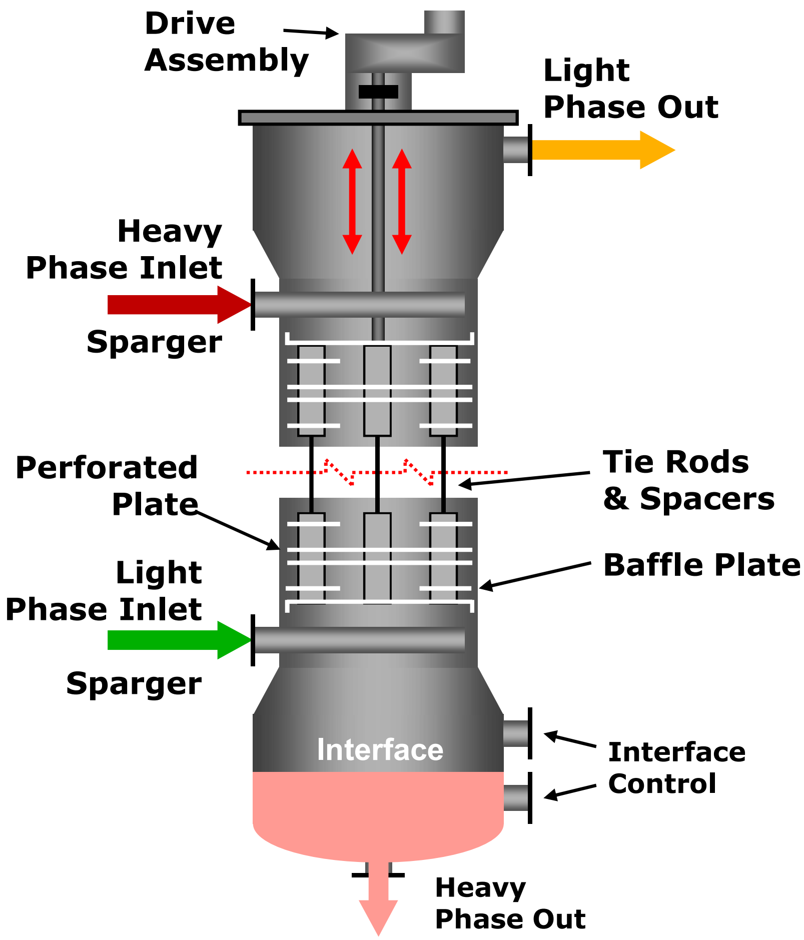
KARR® Reciprocating Column



Characteristics

- Highest capacity:
  - 750-1,500 gal/ft^2-hr
  - 30-60 M^3/M^2-hr
- Good efficiency
- Good turndown capability (4:1)
- Uniform shear mixing
- Best suited for systems that have slow phase separation or emulsify
- Optimal design for systems with suspended solids
- Typical commercial operating speed: 15 – 70 SPM

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KARR® Column Plate Stack Assembly

Internals for a 3 foot (1 meter) diameter KARR® Column

KARR® internals installation

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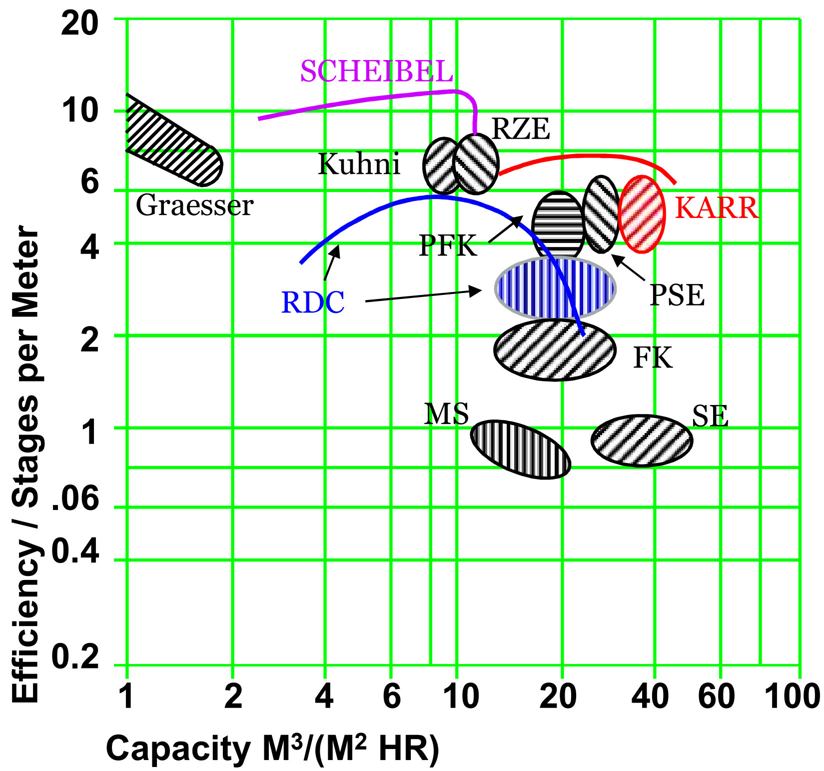
Comparing Commercial Extractors



KEY

Graesser = Raining Bucket
MS = Mixer Settler
SE = Sieve Plate
FK = Random Packed
PFK = Pulsed Packed
PSE = Pulsed Sieve Plate
RDC = Rotating Disc Contactor
RZE = Agitated Cell
KARR = KARR® Recipr. Plate
Kuhni = Kuhni Column
SCHEIBEL = SCHEIBEL® Col.

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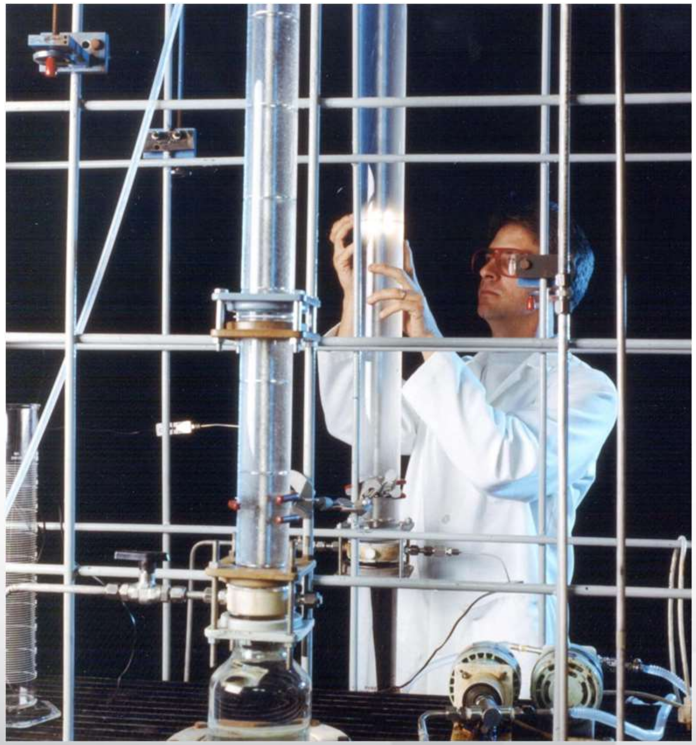
Preliminary LLE Column Design

Required by Koch Modular:

- Mixing and settling behavior of feed and solvent
- Liquid-liquid equilibrium data
- Feed composition and required raffinate composition
- Design capacity – mass feed flow rate and SG

Koch Modular can provide:

- Selection of optimal column type
- Preliminary design (diameter and height)
- Budget cost for extraction column
- Proposal for pilot plant test (required for process performance guarantee)



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Liquid-Liquid Extraction Scale-Up

Theoretical scale-up is difficult due to complex processes occurring in an extractor

- Tendency to Emulsify
- Effects of Impurities or Solids
- Coalescing / Wetting Characteristics
- Phase Ratio Variability and Density Gradients
- Axial and Radial Mixing
- Mass Transfer Rate
- Interfacial and Drop Turbulence Effects

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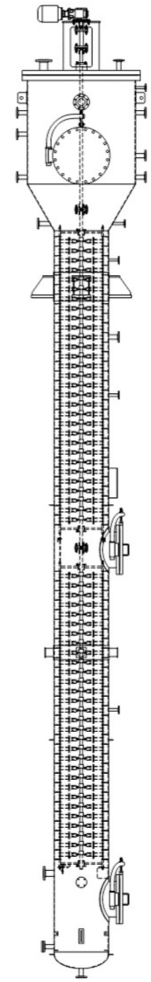
Liquid-Liquid Extraction Scale-Up

Best method of design:
Pilot testing followed by empirical scale-up



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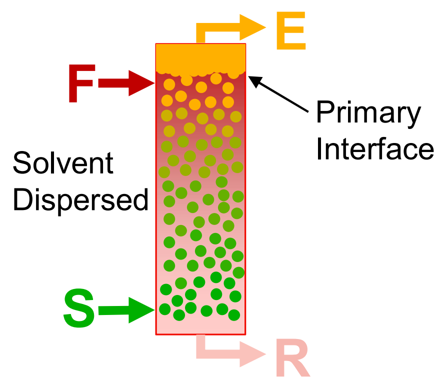
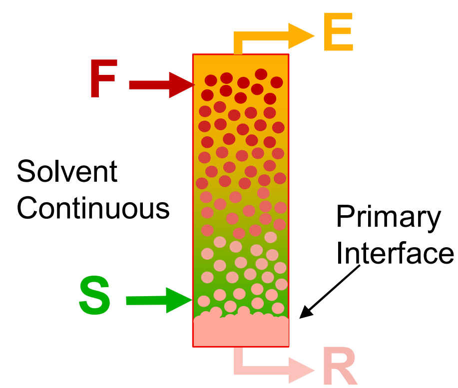
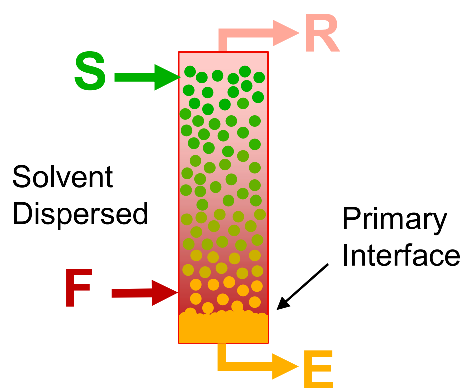
Which Phase is Continuous?

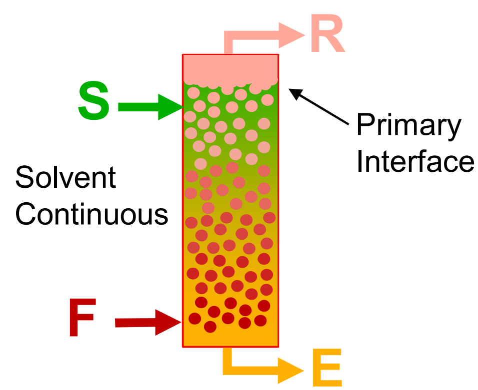
Solvent is Light Phase





Solvent is Heavy Phase





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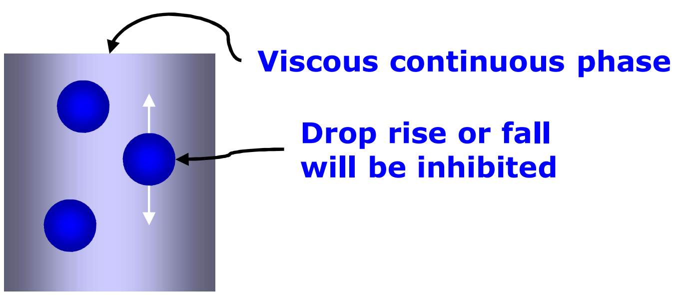
Determining the Dispersed Phase

Flow Rate (Phase Ratio)

- For Sieve Tray and Packed Columns – disperse the higher flowing phase
- For Agitated Columns – disperse lower flowing phase

Viscosity

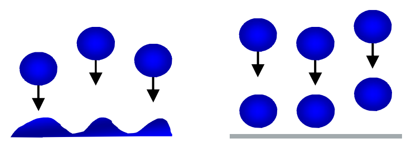
- For efficiency – disperse less viscous phase (greater diffusion in less viscous droplet)
- For capacity – disperse more viscous phase (less drag on droplets)



Surface Wetting

- Want the continuous phase to preferentially wet the internals – this minimizes coalescence and therefore maximizes interfacial area
- **For aqueous-organic systems, if water is the continuous phase, use metal internals, if organic is the continuous phase, use plastic internals**

Droplets coalesce. Interfacial area lost.



Droplets retain shape. Maximizes interfacial area.

Marangoni Effect

- Effect of mass transfer on interfacial tension
- **For greater efficiency, disperse the solvent**
- Droplets tend to repel each other
- Less energy required to maintain dispersion

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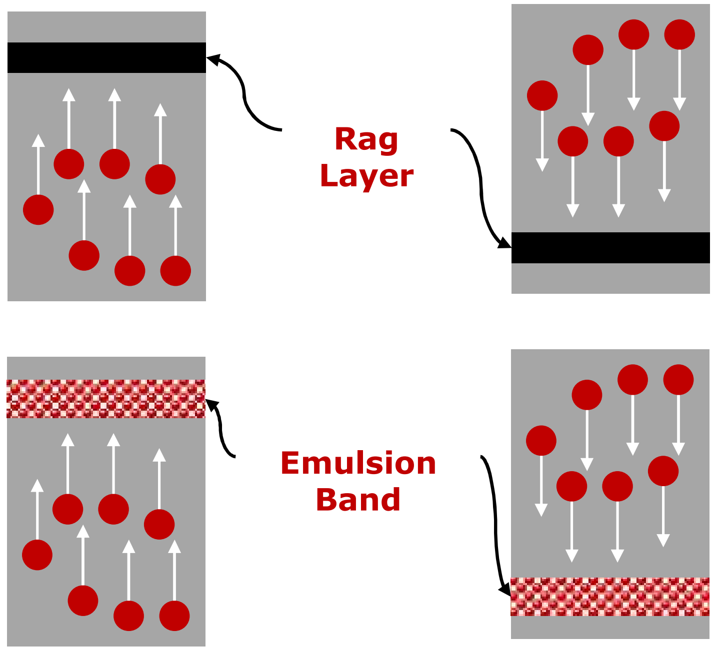
Interface Behavior – Rag Layers and Emulsion Bands

Solids build up at the interface = rag layer

Emulsion band builds up at interface due to slow phase separation



Corrective Actions

1. Reverse Phases
2. For Emulsion Band: slow down capacity or reduce agitation speed
3. For Rag Layer: circulate liquid through an external filter

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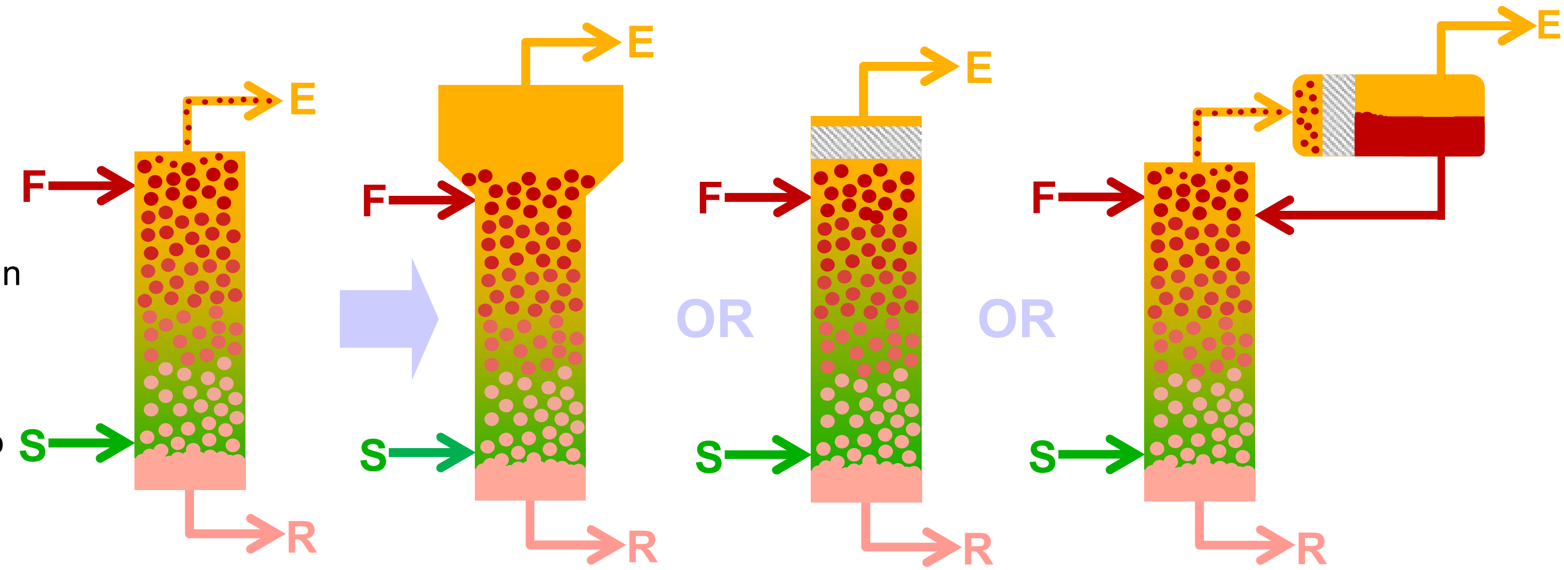
Entrainment

Entrainment refers to removing a small portion of one phase out of the wrong end of the column i.e. where the other phase exits.

Entrainment is controlled by:

1. Increased settling time inside the column
2. Coalescer inside the column, within the disengaging section
3. Coalescer external to the column



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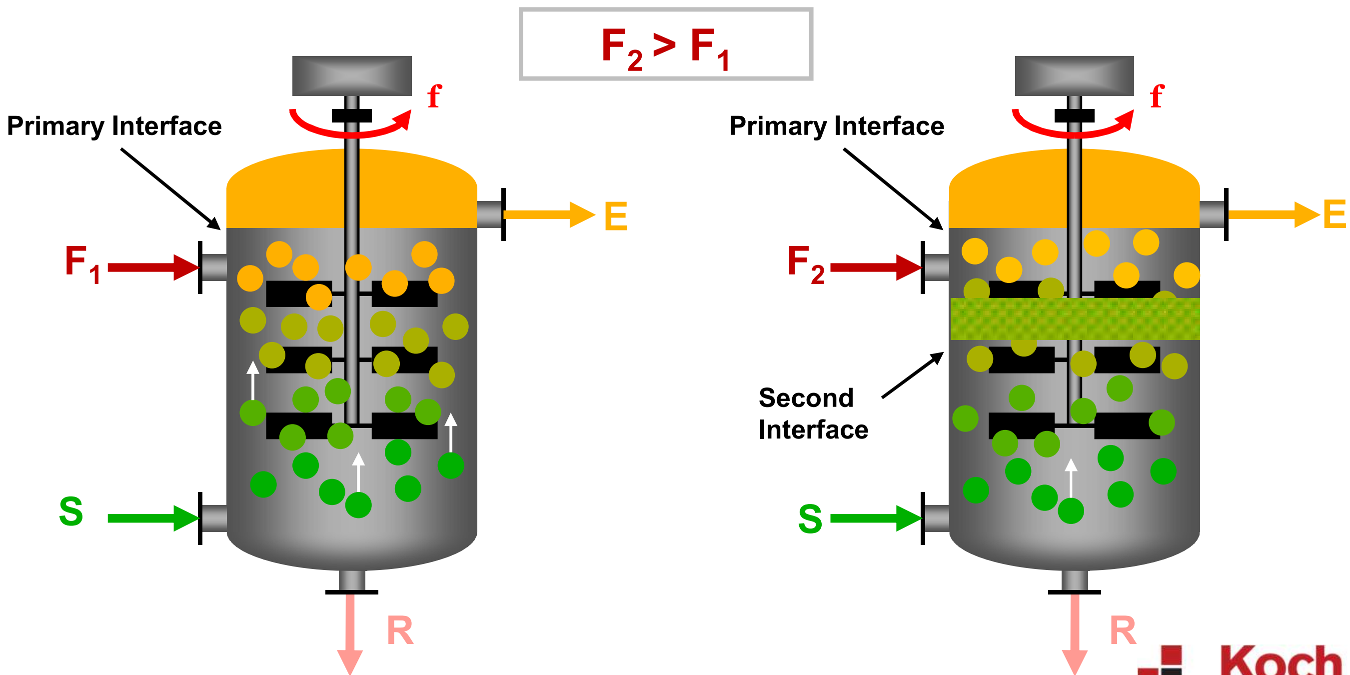
Flooding

Flooding is the point where the upward or downward flow of the dispersed phase ceases and a second interface is formed in the column

Flooding can be caused by:

- **Increased continuous phase flow rate which increases drag on droplets**



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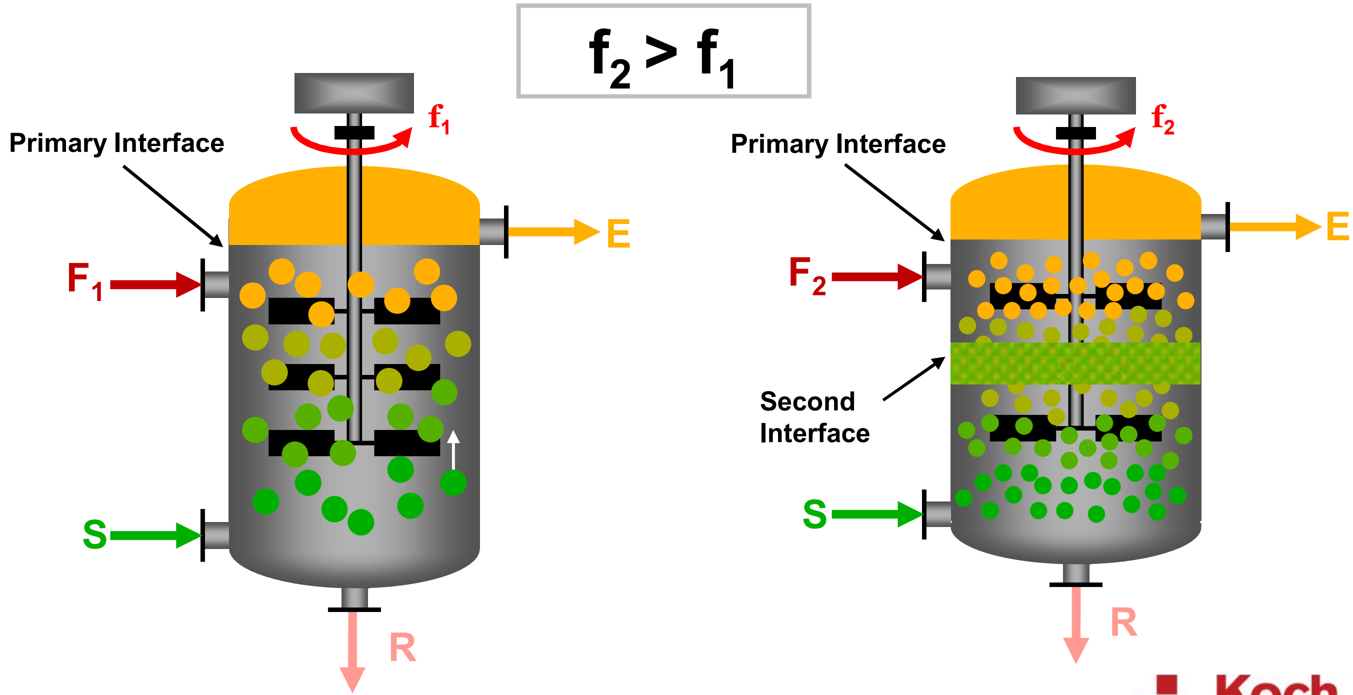
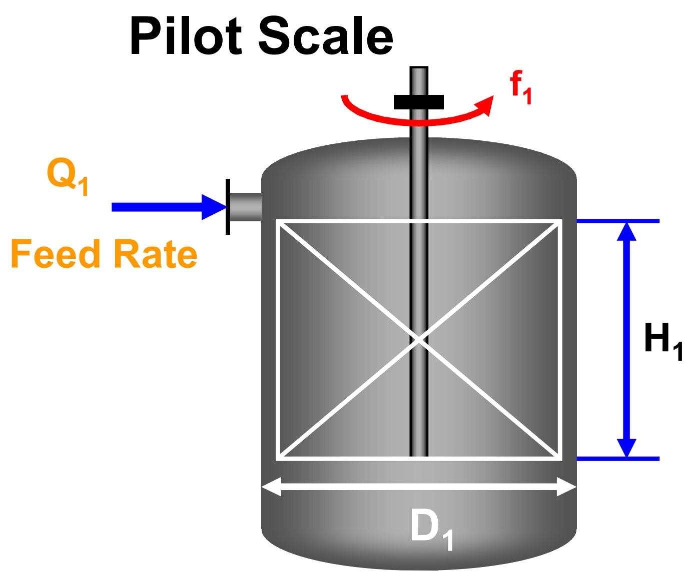
Flooding

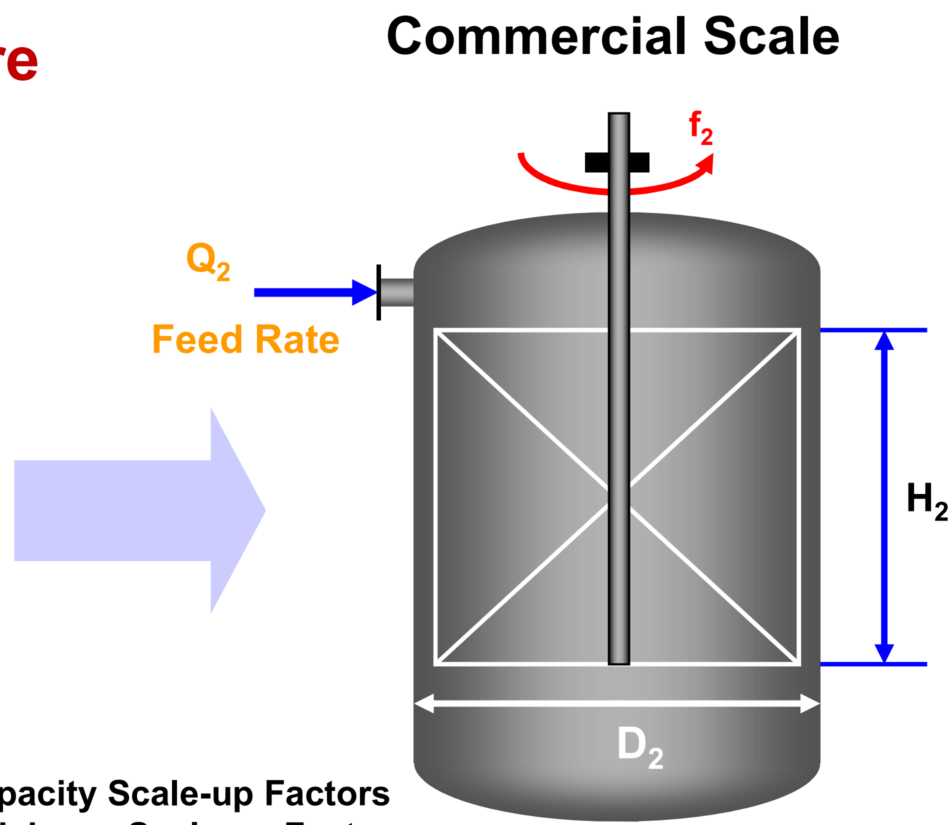
Flooding can be caused by:

- **Increased agitation speed which forms smaller droplets which cannot overcome flow of the continuous phase**
- **Decreased interfacial tension – forms smaller drops – same effect as increased agitation**



Generalized Scale-up Procedure





Basic Scale-up Relationships:

$D_2/D_1 = K_1(Q_2/Q_1)^\wedge M_1$

$H_2/H_1 = K_2(D_2/D_1)^\wedge M_2$

$f_2/f_1 = K_3(D_2/D_1)^\wedge M_3$

Where:

K_1, M_1 = Capacity Scale-up Factors
K_2, M_2 = Efficiency Scale-up Factors
K_3, M_3 = Power Scale-up Factors

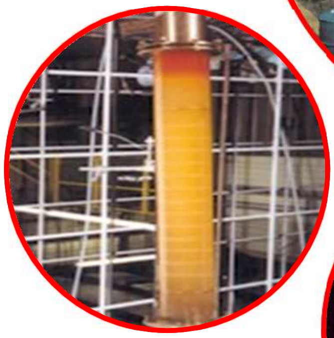
"Axial" or "back" mixing increases as an extraction column's diameter is increased. This phenomena causes concentration gradients that decrease driving force and therefore increase HETS.

Koch Modular Pilot Plant Services Group

Koch Modular maintains a pilot plant dedicated to extraction R & D and applications testing

Pilot Plant Capabilities

- Ability to test liquid-liquid extraction with:
  - KARR® columns with a plate stack as high as 20 feet (6 meters)
  - SCHEIBEL® columns with up to 150 agitated stages
- Distillation for solvent recovery / downstream purification
- Analytical capabilities:
  - GC
  - HPLC
  - Titration
  - IC
  - Karl Fischer
- Outside labs can be used for other types of analysis



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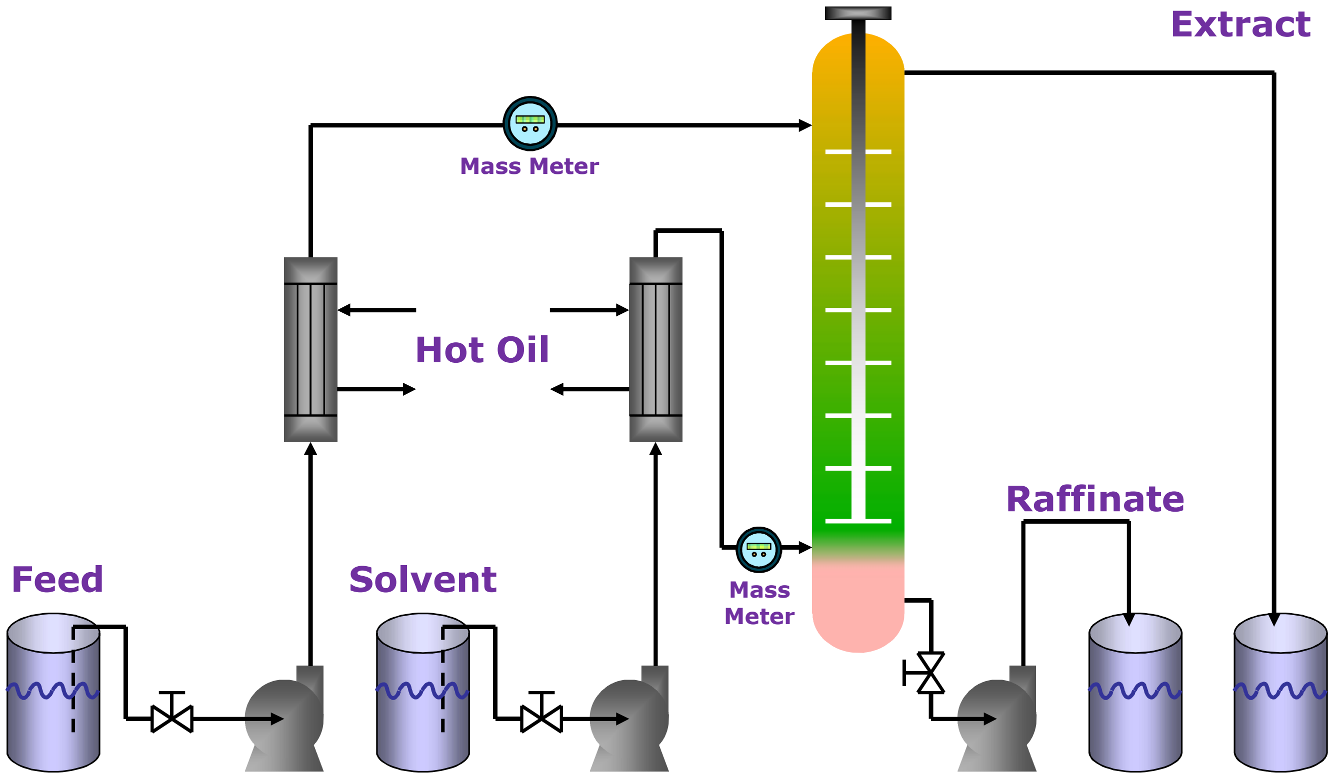
Continuous Extraction Pilot Plant Arrangement



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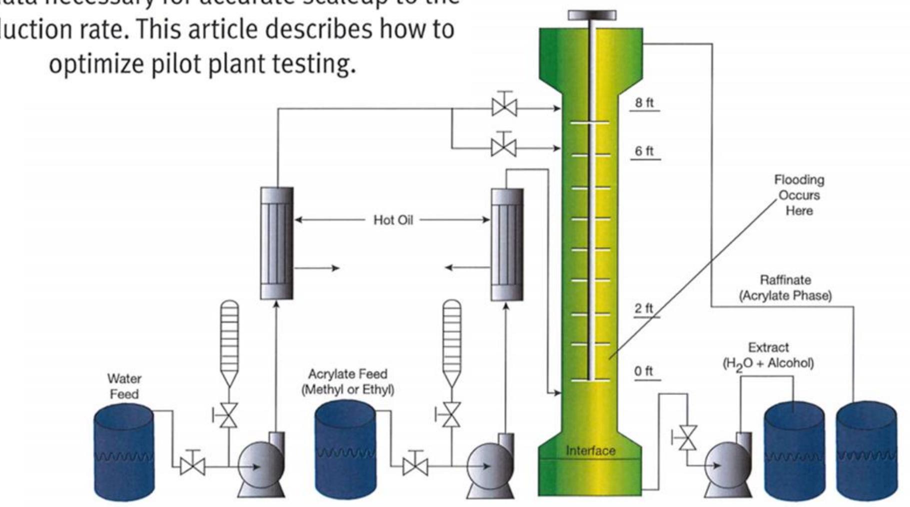
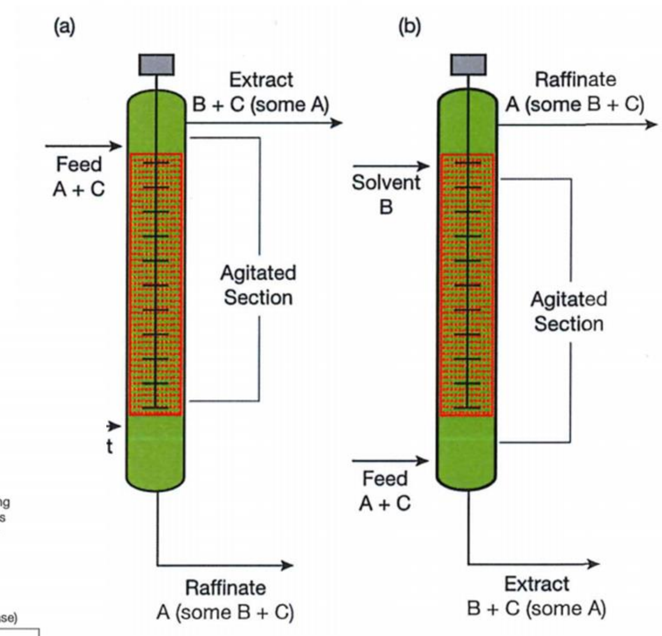
CEP Article February 2018

Pilot Plant Testing for Liquid-Liquid Extraction

Donald J. Glatz
Brendan Cross
Thomas D. Lightfoot, P.E.
Koch Modular Process Systems, LLC

When designing a liquid-liquid extraction column, pilot plant testing generates the data necessary for accurate scaleup to the production rate. This article describes how to optimize pilot plant testing.





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Recovery of Carboxylic Acids from Fermentation Broth

Broth generated from cellulosic materials
– approx. 5% acids
LLE Goal: To achieve >95% recovery (high purity) and minimize solvent usage
Ethyl acetate selected solvent – but emulsified easily

Preliminary Data in RDC Columns

- Difficult operation due to emulsification
- < 90% acid recovery
- High S/F ratio – 2.0

KARR® Column Required

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Pilot KARR® Column for Carboxylic Acids Extraction

1” diameter x 12’ Plate Stack

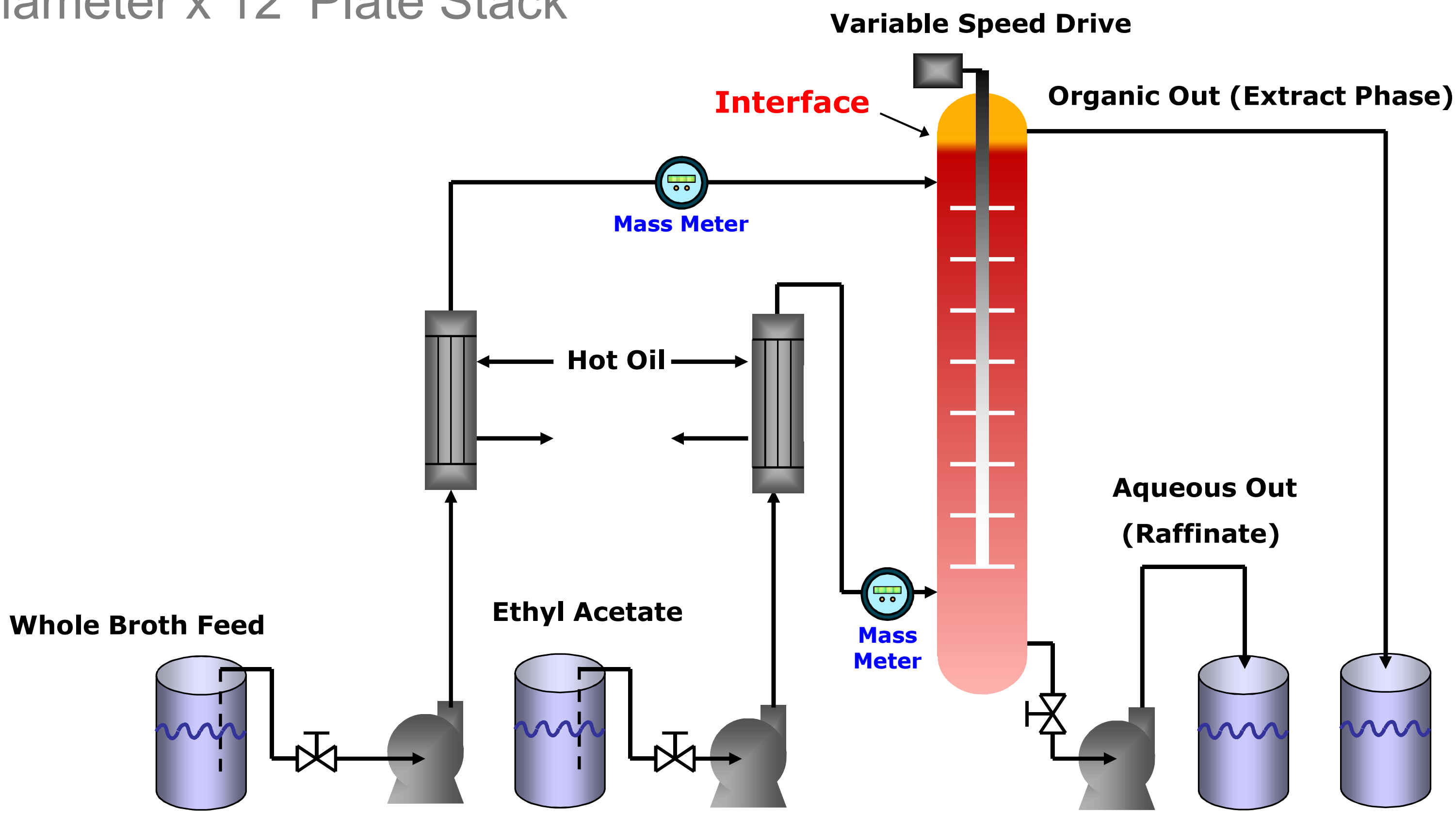

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TABLE 1: Pilot Plant Data for Fermentation Broth Extraction						
All runs performed in a 25 mm diameter, KARR® Column						
RUN	**Plate Stack Ht.**	**Capacity**	**Temp.**	**S/F Ratio**	**Agitation**	**Acid Recovery**
#	**(feet)**	**GPH/ft²**	**C**		**SPM**	**%**
1	12	700	23	1.7	30	95.0
2	12	700	23	1.7	40	97.5
3	12	700	23	1.7	50	Flooded
4	8	700	23	1.7	30	93.3
5	8	700	23	1.7	40	Flooded
6	10	700	23	1.7	30	96.3
7	12	650	23	1.5	30	96.5
8	12	500	23	1.5	40	97.6
9	12	700	23	1.5	30	94.3
10	12	650	45	1.5	30	98.3
11	12	650	45	1.5	50	98.7
12	12	650	45	1.5	60	Flooded

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KARR® Column Pilot Plant Scale-up Procedure

Carboxylic Acid Extraction from Broth

- D_{COMM} = 22" (1:1 Scale-up Based on Capacity)
- $H_{COMM} = (D_{COMM} / D_{PILOT})^{0.38} \times H_{PILOT}$
- $H_{COMM} = (22/1)^{0.38} \times (12 \text{ feet}) = 38 \text{ feet} \mid 11.6 \text{ M}$
- $SPM_{COMM} = (D_{PILOT} / D_{COMM})^{0.14} \times SPM_{PILOT}$
- $SPM_{COMM} = (1/22)^{0.14} \times (50 \text{ SPM}) = 32 \text{ SPM}$
- Where:
  - H_{COMM} = Height Commercial Column
  - H_{PILOT} = Height Pilot Column
  - D_{COMM} = Diameter Commercial Column
  - D_{PILOT} = Diameter Pilot Column
  - SPM_{COMM} = Commercial Strokes Per Minute
  - SPM_{PILOT} = Pilot Strokes Per Minute

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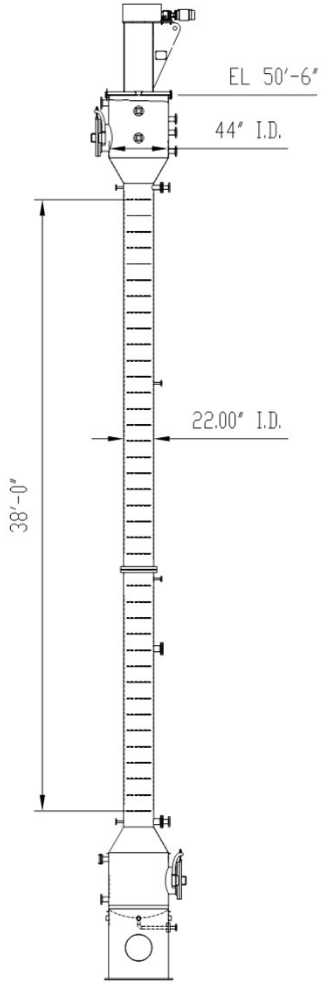
KARR® Column Design | Carboxylic Acids Extraction from Broth



- Diameter = 22" | 0.56M (D_1)
- Expanded Ends
  Diameter = 44" | 1.1M (D_2)
- Plate Stack = 38'-0" | 11.6M (A)
- Overall Height = 50'-6" | 15.4M (B)
- Part of complete modular system (LLE + solvent recovery distillation columns) designed, fabricated, and installed

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Modular System Design | Carboxylic Acids Extraction from Broth

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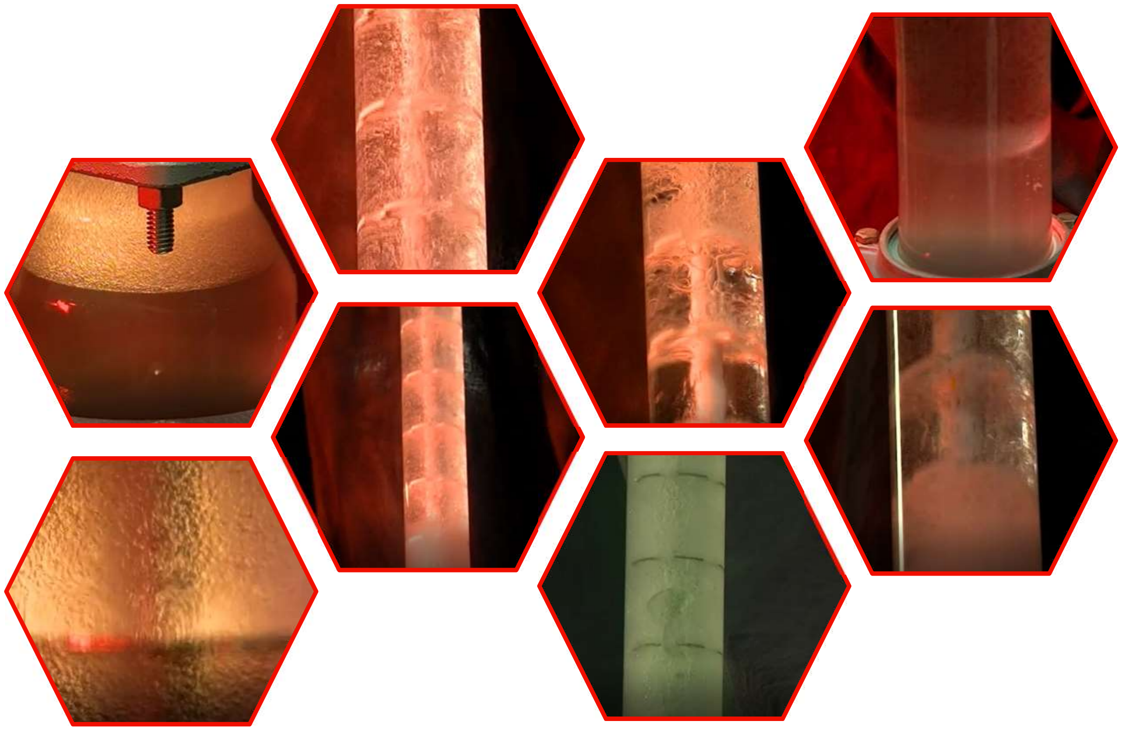
KARR® Column Demonstration Video



Can be viewed on our website or here:
https://www.youtube.com/watch?v=TlJaSK6YEp4

Extraction Experience

Koch Modular has supplied over 300 commercial extraction columns

Koch Modular has also supplied hundreds of pilot scale extraction columns

We have tested more than 200 different processes in the pilot plant

QUESTIONS?

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