Extraction of Chemicals from Fermentation Broths using a KARR® Column

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What We Do

Specialists in Process Design and Construction of Modular Mass Transfer Systems for Solvent Recovery, Wastewater Stripping, Product Purification, Organic Chemical Separations, Acid Gas Treating and Environmental Applications. KMPS also provides engineered components and engineering services, including equilibrium data development, process development and pilot plant testing.

Objective:

Provide economic solutions to separation problems.
Introduction for Presentation

• Recently – large emphasis on production of chemicals from biomass (fermentation, algae)
• LLE is logical preliminary step because chemicals are low concentration & higher-boiling than water
• KARR® Column provides high efficiency and is ideal for these systems because of high tendency towards emulsification
• Presentation outlines LLE for biomass and advantage of the KARR® Column
Fermentation Process with LLE

Fermentation

Solvent Stripping

Liquid-Liquid Extraction

Broth Treatment
Filtration
Centrifuge
Cell Disruption

Distillation (Solvent Recovery)

Additional Dist. Product(s) Purification

Extract

Recycle Solvent

Spent Broth

Recycle Solvent
Liquid-Liquid Equilibrium Data

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

\[
E = \left(\frac{S}{F}\right)M = \left(\frac{50/99}{7.92}\right) = 4.0
\]
Solvent Selection and Generation of Liquid-Liquid Equilibrium Data
LLE Curve for Extraction of Dicarboxylic Acids from a Fermentation Broth

Extract Comp. (Wt. Frac., Solute Free)

Raffinate Composition (Wt. Frac., Solute Free)
Broths Require Many Theoretical Stages

- \( E = m \left( \frac{S}{F} \right) \)
- Chemicals in broth typically have low distribution coefficient (m)
- \( \therefore \) High number of theoretical stages required
- Example: 
  \[ E = m \left( \frac{S}{F} \right) = 0.8(1.63) = 1.3 \]
  10 stages require for 98% recovery
**Selection of Extractor**

**Mixer Settlers**
- Used primarily in the metals industry due to:
  - Large flows
  - Intense mixing
  - Long Residence time
  - Corrosive fluids
  - History

**Column Contactors**
- **Static**
- **Agitated**

**Centrifugal**
- Used primarily in the pharmaceutical industry due to:
  - Low Volume
  - Short Residence time
  - Handles Small Gravity Diff.
  - History

**Spray**
- Rarely used

**Packed**
- Used in:
  - Refining
  - Petrochemicals
  - Example:
    - Random
    - Structured
    - SMVP™

**Tray**
- Used in:
  - Refining
  - Petrochemicals
  - Example:
    - Sieve

**Pulsed**
- Used in:
  - Nuclear
  - Inorganics
  - Chemicals
  - Example:
    - Packed
    - Tray
    - Disc & Donut

**Rotary**
- Used in:
  - Chemicals
  - Petrochemicals
  - Refining
  - Pharmaceutical
  - Example:
    - KARR®
    - SCHEIBEL®

**Reciprocating**
- Used in:
  - Chemicals
  - Petrochemicals
  - Refining
  - Pharmaceutical
  - Example:
    - KARR®

**KARR® and SCHEIBEL® are registered trademarks of Koch-Glitsch, LP.**
Centrifugal Extractor – NOT IDEAL

Centrifugal force is good for phase separation

Disadvantages for Fermentation Broths:
- Insufficient efficiency: typically need too many theoretical stages
- Susceptible to fouling and plugging due to small clearances
- High speed device requires maintenance
Disadvantages for Fermentation Broths:

- Poor efficiency due to poor phase contact: biochemical processes typically require many theoretical stages to achieve product recovery
- Sometime agitation is required to achieve phase separation
- Broths have high tendency to foul and plug
Characteristics with Fermentation Broths:

- High shear causes emulsification – RDC with rotating discs is especially problematic
- Turbine type impellers (e.g. SCHEIBEL® Column) – less shear than RDC but still prone to emulsification
- Non-uniform shear of rotating internals – tip speed creates finer droplet size
- Columns tend to flood before small droplets can be produced and sufficient dispersed phase hold-up is generated
- Not recommended for highly fouling systems
KARR® Reciprocating Column - IDEAL

Characteristics:

- Reciprocating plate stack imparts uniform shear mixing
- Narrow droplet size distribution – does not generate “fine droplets”
- Internals can be metal or plastic to create the proper wetting conditions
- Year of experience show that this type of mixing is best for systems that emulsify
Recovery of Carboxylic Acids from Fermentation Broth

- Broth generated by fermenting cellulosic materials – ~5% acids
- LLE Goal: >95% recovery (high purity) and minimal solvent use
- Ethyl acetate 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
Pilot KARR® Column for Carboxylic Acids
1” diameter x 12’ Plate Stack

Variable Speed Drive

Organic Out
(Extract Phase)

Hot Oil

Aqueous Out
(Raffinate)

Whole Broth Feed

Ethyl Acetate
## Pilot Plant Data for Fermentation Broth Extraction

<table>
<thead>
<tr>
<th>RUN</th>
<th>Plate Stack Ht. (feet)</th>
<th>Capacity (GPH/ft²)</th>
<th>Temp. (C)</th>
<th>S/F Ratio</th>
<th>Agitation (SPM)</th>
<th>Acid Recovery (%)</th>
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<td>700</td>
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<td>650</td>
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</table>

**NOTE:** All runs performed in a 25 mm diameter KARR® Column
Extraction Testing Results

• KARR® Column is correct design for this process which failed in RDC column
• S/F ratio improved to 1.5 (client expected 2)
• 96-97% recovery at room temperature and 98-99% recovery at 40-45 C. Approximately 7 theoretical stages generated.
• Design capacity 650 GPH/ft\(^2\)
• Complete system (LLE + distillations) designed, fabricated, and installed including KARR® Column installed on right
• LLE testing identified “unknown” component
Recovery of Carboxylic Acids from Broths Using a Low Boiling Solvent

Fermentation Broth
5% carboxylic acids

Solvent: Ethyl Acetate

Extract

Recycled Ethyl Acetate

Extraction

Raffinate

Stripping

Aqueous Raffinate

Recovery

Carboxylic Acids
Application: Extraction of Algae Oil

Recovery of “oil” from broth generated in algae pond
Requirement - >95% recovery of oil
Minimization of solvent usage critical to economics (solvent recovery)

Preliminary Data in Mix-Decant (Batch)
• Extremely prone to emulsification
• Large solvent usage due to multiple mix-decant steps
• Poor phase separation caused large solvent loss and generation of waste

KARR® Column required
## Pilot Plant Data for Algae Broth Extraction

All runs performed in a 25 mm diameter, KARR® Column

<table>
<thead>
<tr>
<th>RUN</th>
<th>Plate Stack Ht.</th>
<th>Capacity</th>
<th>Temp.</th>
<th>S/F Ratio</th>
<th>Agitation</th>
<th>Oil Recovery</th>
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<td>°C</td>
<td></td>
<td>SPM</td>
<td>%</td>
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</tbody>
</table>
Summary – Algae Oil Extraction

• KARR® Column is the correct design for this process – good phase separation.
• At 500 GPH/ft² & 12’ plate stack height, 98% recovery achieved for S/F ratio = 0.5 -1.0
• Product recovery decreased for plate stack height of 8’
• Product recovery decreased at 700 GPH/ft² and column was unstable at 900 GPH/ft.
• Demonstration plant column designed with fabrication pending.
Conclusions

- LLE is excellent first step for recovery and purification of chemicals from broths created by fermentation, algae or other biomass processing.
- Agitated columns are required in order to generate sufficient theoretical stages for high product recovery and minimization of solvent usage which is important for process economics.
- Agitation via reciprocation (KARR® Column) is the optimal choice for system that emulsify.
Thank You!

QUESTIONS???
LLE Equilibrium and Operating Lines

Solute Free Basis

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

Graphical Solution

- $Y_{BE} = \frac{y_{BE}}{y_{AR} + y_{CE}}$
- $X_{BR} = \frac{x_{BR}}{x_{AR} + x_{CR}}$

Equations:

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

Operating Line: $S' / F' = m$

Equilibrium Curve: $Y_{BE} / X_{BR} = m$

Distribution Coefficient on Solute Free Basis: $m = \frac{Y_{B}^{*}}{X_{B}^{*}}$
DCA Extraction – Theoretical stage calculation for 98% extraction at solvent to feed ratio of 1.0

Extract Comp (Wt Frac., Solute Free)

Raffinate Composition (Wt Frac., Solute Free)

(0.136, 0.118)