A novel TOA-glycerol based extraction-re-extraction process for the separation of chemicals produced by acidogenic fermentation of biomass

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Ethanol and volatile fatty acids can be produced by acidogenic fermentation.

Fermentable Biomass → Acidogenic fermentation → Fermentation broth → Water, Ethanol, Acetic, propionic, butyric and lactic acids
Concentrating ethanol and acids is necessary

- Acidogenic fermentation advantages:
  - Non-axenic conditions
  - Any fermentable biomass
  - Non-pretreated biomass

- Acidogenic fermentation limitations:
  very diluted aqueous solutions (+/- 1% organic acids) produced

Separating and concentrating the molecules is essential
Development and optimisation of an efficient process for the separation of organic acids from the fermentation broth

Fermentation broth

\[\text{SEPARATION}\]

Acetic, propionic, butyric, lactic acids
Ethanol
Outline

- Separation process
- Experimental study
- Modeling
- Conclusions and perspectives
Liquid-liquid extraction seems to be the most promising technique

- Technique for the lactic acid: precipitation
  Expensive and non environment-friendly

- Other separation techniques
  - Distillation
    Large water flow to evaporate
  - Vapor permeation
    Large water flow to evaporate
  - Pervaporation
    Large water flow to evaporate
    No available membrane
  - Electrodialysis
    Unefficient use of electric energy
  - Extraction PROMISING OPTION
Complete process based on two liquid-liquid extraction columns.
Outline

- Separation process
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- Conclusions and perspectives
Distribution coefficient:

\[ K_D = \frac{x_A^{\text{extract}}}{x_A^{\text{raffinate}}} \]

Experimental approach
Operating parameters strongly influence the distribution coefficient

- Type of carboxylic acid
- pH
- Temperature

Used solvent: Pure tri-n-octylamine (TOA)
Extraction efficiency is highly influenced by the composition of the solvent.

**Diagram Description:**
- **FERMENTATION BROTH WATER + ACIDS**
- **SOLVENT + ACIDS**
- **GLYCEROL**
- **GLYCEROL + ACIDS**
- **SOLVENT**

**Graphs:**
- **KD solvent/water**
- **KD glycerol/solvent**

**Graph Legend:**
- TOA + dodecanol
- TOA + dodecanol + hexane
- TOA + TBP
- TOA
- TOA + TPeA

**Additional Information:**
- TOA: Tri Octyl Amine
- TBP: Tri n-Butyl Phosphate
- TPeA: Tri Pentyl Amine
Outline

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Modeling

- Software simulating a countercurrent multistages liquid-liquid extraction column
  - Mass balances
  - Phase equilibria
    - $K_D$
    - Solubilities

- Data: experimental distribution coefficients and solubilities
Simulations of the extraction-reextraction 2 steps process

1 stage

Stage 1

Feed → Extract → Raffinate

Solvent → Raffinate → Glycerol

Extract → Glycerol+ acids

2 stages

Stage 1

Feed → Extract → Raffinate

Solvent → Raffinate → Glycerol

Stage 2

Extract → Glycerol+ acids

Graphs show the extraction degree (%) for different solvents:
- TOA+Dodecanol
- TOA+Dodecanol+Hexane
- TOA+TBP
- TOA
- TOA+TPeA

Graph on the left: Extraction degree (%) from 0 to 35.
Graph on the right: Extraction degree (%) from 0 to 35.
Extraction degree for the 1st extraction as a function of number of stages
Extraction degree for the extraction – reextraction process

10 stages for each extraction column
Which solvents are less efficient for the first extraction?
Next step: extraction with vegetable oils

Table 2. Distribution Coefficients of Butyric Acid for Different Solvents Tested at $T = 298.15$ K$^a$

<table>
<thead>
<tr>
<th>solvent type</th>
<th>solvent</th>
<th>$D$</th>
<th>$C_{BA(aq)}$</th>
<th>literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>vegetable oil</td>
<td>hazelnut oil</td>
<td>1.08</td>
<td>0.468</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>corn oil</td>
<td>1.08</td>
<td>0.462</td>
<td>this study</td>
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<tr>
<td></td>
<td>soybean oil</td>
<td>1.08</td>
<td>0.469</td>
<td>this study</td>
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<td></td>
<td>olive oil</td>
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<td></td>
<td>sunflower oil</td>
<td>0.99</td>
<td>0.523</td>
<td>ref 6</td>
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<tr>
<td></td>
<td>rape seed oil</td>
<td>1.02</td>
<td>0.510</td>
<td>ref 6</td>
</tr>
</tbody>
</table>

$^a C_{BA(aq)}$, butyric acid concentration at equilibrium in aqueous phase.

Bilgin, et al. (2006) *Distribution of butyric acid between water and several solvents*, Journal of Chemical and Engineering Data, 51, pp 1546-1550

low distribution coefficients
Conclusions and perspectives

- Operating conditions and solvents screening
- Fermentation broth
- Efficiency of the process at the industrial scale
- Verification on a pilot equipment