Biofuels Production from Volatile Fatty Acid Platform

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What are VFAs?

: Volatile Fatty Acid, carboxylic acid with less than C6

- No need sterilization
- No additional hydrolysis enzyme
- Mixed culture
- Acidogenesis : fast
- Methanogenesis : slow

![Diagram showing the process of VFAs formation and biogas production](image)
VFA-based Biofuels

1. Pretreatment (lignin: little, regular)
2. VFA (slow ➔ high rate)
3. Concentration of VFAs (30g/L ➔ 400g/L)
   - Evaporation (25kwh/m³ ton of water)
   - Solvent extraction (efficiency ➔ durability)
4. Hydrogenation (catalytic, 200°C, 20 atm)
   - \( \text{CH}_3\text{COOH} + 2\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \)
   - Propionic acid + 2H₂ ➔ propanol + H₂O
   - Butyric acid + 2H₂ ➔ butanol + H₂O
5. Separation to ➔ ethanol, propanol, butanol
VFA Platform

**Principle**
- Disintegration
  - Hydrolysis
    - extracellular enzymatic process
  - Fermentation & Anaerobic Oxidation
  - Acetogenesis & Hydrogenesis
- VFAs
  - Biological & thermochemical process
  - Gas, Liquid Biofuels, Biochemicals

**Application**
- Raw Materials
  - Anaerobic digestion
  - VFAs
  - C2: Acetate
  - C3: Propionate
  - C4: Butyrate
  - C5: Valerate
  - C6: Caproate

**Gas BioFuels**
- Methane
- BioHydrogen
- Ethanol
- Butanol
- Microbial Biodiesel

**BioChemicals**
- Bioplastics
- Bulk chemicals (C3 - C6)
- Pharmaceuticals
- Textiles
- Other value added chemicals

Production Routes of Fuel Alcohols

Fermentation: one of the key technologies in biological conversion

- **Biomass**
  - Hydrolysis
  - Gasification
- **Sugars**
  - Fermentation (80 gal/ton)
- **Syngas**
  - Fermentation (56 gal/ton)
  - Catalysis
- **VFA**
  - Fermentation (85 gal/ton)
  - Catalysis
- **Acetate**
  - Thermal conversion, Catalysis
- **Ethanol**
  - (current yield in pilot-scale)
- **Mixed Alcohol**
  - (120 gal/ton)

*VFA: volatile fatty acid*
Liquid Biofuel Costs (2005~2030)

- Ethanol
- Diesel

Daily market offer prices for petroleum products at several global locations from 3 January 2005 till 6 April 2006

- Biofuel cost (2006~2030)

- Fischer Tropsch
- Ligno cellulose
- Vegetable oils
- Animal fats
- Sugar cane
- Corn
- Wheat
- Beet

Source:

Ethanol

Biofuel
Cost Comparison

Ethanol Production Cost ($/L)

(Sugar platform) ¹) (VFA platform) ²)

Sugarcane ¹) Corn ¹) Lignocellulose

¹) Estimated by IEA/OECD, 2006
²) Estimated by M. Holtzapple, 2009
Demand for New Process Development

Flexible application to various biomass

- Organic wastes
- Agricultural wastes
- Forest residues
- Energy crops
- Marine biomass
- MSW

Cost effective process

- No sterility
- No GMOs
- Adaptable
- No pure cultures
- Low capital
- No enzymes
- High product yields
- No vitamin addition
- Co-products not required

Requirement of new biorefinery platform less sensitive to species, composition, and water content of biomass
Search for New Biofuel Platform

1. Abundant Raw Materials in Korea and in other countries.
   - Materials with negative cost: foodwaste, sewage sludge, fallen leaves and other biodegradable organic wastes

2. Do I have a good technology and experience?
   - Fermentation with high cell density culture (1982~)
   - Foodwaste treatment since 1996

3. The cost of production should be competitive,
   - vs. existing biofuels (sugar cane, grain-based; $100 bbl-oil)
   - Even at a smaller scale, the product should be marketable so that technology development may go on.

My group started biofuel research in 2005.
We came to a conclusion. → VFA-platform
### Mass

**Alcohol production from lignocellulosic biomass**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pretreat.</th>
<th>Hydrolysis</th>
<th>C6 ferment.</th>
<th>C5 ferment.</th>
<th>Recovery</th>
<th>Sum EtOH</th>
<th>Total EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulosic Ethanol (Sugar platform)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>38%</td>
<td>→</td>
<td>90%</td>
<td>90%</td>
<td>51%</td>
<td>95%</td>
<td>14.91%</td>
</tr>
<tr>
<td>C5</td>
<td>27%</td>
<td>→</td>
<td>90%</td>
<td>90%</td>
<td>51%</td>
<td>95%</td>
<td>10.60%</td>
</tr>
<tr>
<td>Lignin</td>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>12%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pretreat.</th>
<th>Anaerobic digestion</th>
<th>VFA recovery</th>
<th>Hydrogen Rxn</th>
<th>Sum Alcohol</th>
<th>Total Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed Alcohol (VFA platform)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>38%</td>
<td>→</td>
<td>90%</td>
<td>76%</td>
<td>95%</td>
<td>77%</td>
</tr>
<tr>
<td>C5</td>
<td>27%</td>
<td>→</td>
<td>90%</td>
<td>76%</td>
<td>95%</td>
<td>77%</td>
</tr>
<tr>
<td>Lignin</td>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>12%</td>
<td>→</td>
<td>90%</td>
<td>30%</td>
<td>95%</td>
<td>77%</td>
</tr>
</tbody>
</table>

### Money

**Cellulosic Ethanol**

Return $ = 0.3/kg(EtOH) * 0.2551/kg biomass = $0.0765/kg biomass (Biomass cost = 52.3%)

**Mixed Alcohol**

Return $ = 0.3/kg(EtOH) * 0.3489/kg biomass = $0.105/kg biomass (Biomass cost = 38.1%)

* Biomass price = $40/tonne

### Energy

**Cellulosic Ethanol**

$Y = 25.51\% \rightarrow 26.84 \text{ MJ/kg} * 0.2749 \text{ kg/kg} = 7.28 \text{ MJ/kg biomass}$

**Mixed Alcohol**

$Y = 34.89\% \rightarrow 30.2 \text{ MJ/kg} * 0.3489 \text{ kg/kg} = 10.54 \text{ MJ/kg biomass} (9.28 \text{ MJ/kg})$

1 Ethanol:Propanol:Butanol = 6:1:3
2 $H_2$ consumption = - 120 MJ/kg * 0.3489 * 0.03 g $H_2$/g alcohol = - 1.256 MJ
Korean Foodwastes

Foodwastes Composition

<table>
<thead>
<tr>
<th>Item</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solid(TS), [%]</td>
<td>21</td>
</tr>
<tr>
<td>Volatile Solid(VS), [%]</td>
<td>83</td>
</tr>
<tr>
<td>Fibers in TS, [%]</td>
<td>7.05</td>
</tr>
<tr>
<td>Lipids in TS, [%]</td>
<td>15.5</td>
</tr>
<tr>
<td>Proteins in TS, [%]</td>
<td>17</td>
</tr>
<tr>
<td>Carbohydrates in TS, [%]</td>
<td>40</td>
</tr>
</tbody>
</table>

(Average values of Korean foodwastes)

Amount of producible alcohols

<table>
<thead>
<tr>
<th>Sugar platform</th>
<th>VFA platform</th>
</tr>
</thead>
<tbody>
<tr>
<td>(% of TS)</td>
<td>(% of TS)</td>
</tr>
<tr>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>20</td>
<td>22.5</td>
</tr>
</tbody>
</table>

Sum: 23.5 < < 42.8

- Usually organic wastes have high protein and lipid content.
- Especially VFA platform is suitable for organic wastes.
VFA Fermentation

- VFAs production from foodwates at HRT = 12 days

### VFA Composition Control

#### Temperature

<table>
<thead>
<tr>
<th>Effect of temperature on acidogenesis of food wastes</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>30,500–32,500</td>
</tr>
<tr>
<td>TVFA (g/L)</td>
<td>16.5–17.5</td>
</tr>
<tr>
<td>Acetate (g/L, %)</td>
<td>3.00–3.50</td>
</tr>
<tr>
<td>Propionate (g/L, %)</td>
<td>7.30–8.00</td>
</tr>
<tr>
<td>Butyrate (g/L, %)</td>
<td>4.40–46.0</td>
</tr>
<tr>
<td>Valerate (g/L, %)</td>
<td>2.40–2.70</td>
</tr>
<tr>
<td>Caproate (g/L, %)</td>
<td>3.00–3.20</td>
</tr>
<tr>
<td>Succinate (g/L, %)</td>
<td>1.82–19.2</td>
</tr>
<tr>
<td>NH₄⁺–N (mg/L)</td>
<td>1.0–4.0</td>
</tr>
<tr>
<td>PO₄³⁻–P (mg/L)</td>
<td>40.0–50.0</td>
</tr>
<tr>
<td>Yield (VFA/VFs₀)</td>
<td>0.24–0.26</td>
</tr>
<tr>
<td>Productivity (g VFA/L d)</td>
<td>2.06–2.19</td>
</tr>
</tbody>
</table>

#### pH

<table>
<thead>
<tr>
<th>Effect of pH on acidogenesis of food wastes</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>SCOD (mg/L)</td>
<td>27,000–29,000</td>
</tr>
<tr>
<td>TVFA (g/L)</td>
<td>15.0–18.0</td>
</tr>
<tr>
<td>Acetate (g/L, %)</td>
<td>2.50–3.00</td>
</tr>
<tr>
<td>Propionate (g/L, %)</td>
<td>0.50–0.70</td>
</tr>
<tr>
<td>Butyrate (g/L, %)</td>
<td>2.60–3.70</td>
</tr>
<tr>
<td>Valerate (g/L, %)</td>
<td>16.3–18.4</td>
</tr>
<tr>
<td>Caproate (g/L, %)</td>
<td>0, 0</td>
</tr>
<tr>
<td>Succinate (g/L, %)</td>
<td>1.70–2.00</td>
</tr>
<tr>
<td>NH₄⁺–N (mg/L)</td>
<td>0.52–0.97</td>
</tr>
<tr>
<td>PO₄³⁻–P (mg/L)</td>
<td>6.50–8.50</td>
</tr>
<tr>
<td>Yield (VFA/VFs₀)</td>
<td>1.3–10.9</td>
</tr>
<tr>
<td>Productivity (g VFA/L d)</td>
<td>1.88–2.25</td>
</tr>
</tbody>
</table>

- High temperature: increase of acetate concentration and ratio
- High pH: increase of short chain VFA
- Controllability of VFA composition
Treatable Biomass

**Low lignin biomass** (no pretreatment need)
- Agricultural organic wastes
- Sludge
- Food wastes
- Manure
- Marine biomass
- All biodegradables

**High lignin biomass** (need pretreatment)
- Woods (forest wastes)
- Agricultural wastes
- Energy crops
Biomass is mainly composed of carbohydrates, lipids, and proteins. And many biomasses are the complex of biomass with various composition. Using the sugar part of biomass mixture, especially wetted organic wastes, is wasteful and needs the large wastewater treatment facilities. The VFA platform may be a modified form of biogas platform to diversify producible products, most part of biomass is converted to simple acids, and do not need additional enzymes.
## Sugar Platform versus VFA Platform

<table>
<thead>
<tr>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sugar platform</strong></td>
<td>Only use sugars part of biomass</td>
</tr>
<tr>
<td>Favorable substrate for microbes</td>
<td>High sugar price</td>
</tr>
<tr>
<td>High energy potential</td>
<td>High enzyme cost</td>
</tr>
<tr>
<td>High inhibitory concentration</td>
<td>Sugar uptake specificity (C5 &amp; C6)</td>
</tr>
<tr>
<td><strong>VFA platform</strong></td>
<td>Unfavorable substrate for microbes</td>
</tr>
<tr>
<td>Use all biomass (wastes)</td>
<td>Unfavourable substrate for microbes</td>
</tr>
<tr>
<td>Low acids production cost</td>
<td>Low chemical energy level of VFA</td>
</tr>
<tr>
<td>No enzyme addition</td>
<td>Relatively high inhibition to microbes</td>
</tr>
<tr>
<td>High VFA yield</td>
<td></td>
</tr>
<tr>
<td>Hydrogen coproduction</td>
<td></td>
</tr>
<tr>
<td>No sterilization</td>
<td></td>
</tr>
<tr>
<td>Less CO₂ emission than sugar-P</td>
<td></td>
</tr>
</tbody>
</table>
Major Bottlenecks in VFA Platform

VFA production

- Pretreatment of biomass (lignin removal)
- Low acid concentration (~ 30 g/L)
- Productivity enhancement (higher than 1 g/L/hr)
- VFA recovery from dilute fermentation broth
  - Distillation
  - Solvent extraction
- Inhibition of methane formation

Chemical route

- Catalysts (e.g. hydrogenation, hydrogenolysis)
- Catalysts life cycle

Biological route

- Strain development and fermentation
- Metabolic engineering for acid uptake and conversion (e.g. biohydogenation)
MixAlco Process Plant

Terrabon Semi-Works Plant
Football field = 1.32 acres
Terrabon Semi-Works Plant = 1.43 acres

- Capacity: five dry tons biomass/day
- Too large land area for pretreatment and fermentation
Fermentation Productivity

\[ Q_p \ (g\text{-product/L.h}) \]

**Specific cell productivity**
- \( q_{p/X} \) : (g-product/g-cell•h)

**Cell concentration**
- \( X \) (g-cell/L)

**Substrate availability**
- \( Y_{P/S} \) (g-p/g-s)

**Inhibitor removal**
- \( K_I \)

**Strain Development**
- Mutation, Screening
- Metabolic engineering
- Directed Evolution

**Impact : variable**

**HCDC**
- Cell recycle
- Immobilization
- Perfusion

**Impact : 4~40 fold**

**Feeding**
- Batch, fed-batch
- Continuous
- Air
- Oxygen recycle
- *in situ* separation

**Impact : variable**

---

Impact : variable
High Efficiency Fermentation Technology

**MSC-HCDC**: Multistage Continuous High Cell Density Culture

<table>
<thead>
<tr>
<th>Modes of Operation</th>
<th>Batch, Fed-batch</th>
<th>Continuous culture</th>
<th>Proposed MSC-HCDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell conc.</td>
<td>10</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Product titer</td>
<td>100</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Productivity</td>
<td>1</td>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>

Examples
- Monoclonal antibody
- Lactic acid
- Ethanol
- Ground food waste treatment
Methods of VFA Recovery

Concentration (water removal)

- **Phase change**
  - Distillation (MSF, ME, VC, Solar) : heat energy
  - Freezing (FD) : cold energy
- **Membrane**
  - Reverse osmosis (RO, NF) : pressure difference (mechanical)
  - Electro-dialysis (ED) : electrical energy

- **Water extraction**
  - Amine dewatering

VFA purification

- Solvent extraction (amine solvent)
- Back-extraction
- Distillation (reactive distillation)
Efficient Water Distillation

**MSF: Multiple-Stage Flash Distillation**

**MED: Multi-Effect Distillation**

**VCD: Vapor Compression Distillation**

Source: www.roplant.org
Water Distillation Energy

- Heat One kg Water to 100°C = 418 kJ/kg
- 1 kWh = 3600 kW-sec = 3,600kJ
- One kWh Gives 3600/418 = 8.6 kg Water
- One kWh Gives 8.6 kg = 8.6 liter Water (116.3 kWh/m³)
- Cost at 8 cents/kWh: 0.93 cents/liter ($0.93/m³)
- Cost must be reduced (by one tenth).

Efficient Water Separation Methods

- RO : Reverse Osmosis
- MSF : Multi-Stage Flash
- ME : Multi-Effect Distillation
- VC : Vapor Compression Distillation
- ED : Electro-Dialysis

Distillation cost : < $2/m³

Source: Park SJ, KIMM, 2007
Catalysts for Alcohol Synthesis

- **Hydrogenolysis catalysts**
  - VFA ester conversion to alcohols

- **Copper chromite**
  - high temperatures (> 200°C)
  - high pressures (> 600 psi) (> 40.8 atm)
  - widely used in industry (e.g., for making detergent alcohols from fatty acids)

- **Reduced CuO-ZnO catalyst**
  - low temperature (~150°C)
  - low pressure (<350 psi) (< 23.8 atm)
  - preferred
Thank you for your attention.

Question?