Oil Refinery

- Crude Oil: $431/ton, $66/bbl, $1.57/gal
- Chemicals: $566/ton, $73/bbl, $1.73/gal
- Fuels: $66/bbl, $73/bbl, $1.73/gal
- Polymers: $566/ton, $73/bbl, $1.73/gal
Biomass Refinery

- Biomass
  - $40/ton
  - $15/bbl*
  - $0.36/gal*

- Feed
  - Equivalent energy basis

- Food

- Chemicals
  - $362 – 543/ton
  - $50 – 75/bbl
  - $1.20 – 1.80/gal

- Fuels

- Polymers

- Fiber

- Pharmaceuticals

* Equivalent energy basis
Chemicals: Thermochemical platform

Lignocellulose \( \xrightarrow{\text{Gasify}} \) CO \( \xrightarrow{\text{H}_2 \text{Catalyst}} \) Chemicals
(Syngas)

- Fischer Tropsch fuels
- Methanol
- Mixed alcohols
- Ammonia
Chemicals: Thermochemical platform

Lignocellulose $\xrightarrow{\text{Gasify}}$ CO $\xrightarrow{\text{Catalyst}}$ H$_2$ (Syngas) $\xrightarrow{}$ Chemicals

- Fischer Tropsch fuels
- Methanol
- Mixed alcohols
- Ammonia

Disadvantages

- 30–40% biomass energy lost to heat
- Must couple to electricity markets
- Expensive gasifiers
- Complex downstream processing
- Difficult to supply enough biomass to achieve economy of scale
Chemicals: Sugar platform

Corn → Sugars → Chemicals
Enzymes
Microorganism
Squeeze

Sugarcane

Ethanol
Butanol
Acetone
2,3 Butanediol
Glycerol
Acetoin
Acetic acid
Lactic acid
Propionic acid
Succinic acid
Butyric acid
Citric acid
Chemicals: Sugar platform

Disadvantages

- Limited availability
- Competition with food
- Requires sterility
- Difficult separations
Chemicals: Sugar platform
(2nd Generation)

Lignocellulose ➔ Sugars ➔ Chemicals

Enzymes

Microorganism

Ethanol
Butanol
Acetone
2,3 Butanediol
Glycerol
Acetoin
Acetic acid
Lactic acid
Propionic acid
Succinic acid
Butyric acid
Citric acid
Chemicals: Sugar platform (2nd Generation)

Lignocellulose → Sugars → Chemicals

Enzymes → Microorganism

Disadvantages

- Requires sterility
- Expensive enzymes
- Difficult to use all sugars
- Uses GMOs
- Lignin not converted to liquid fuels
- Extensive pretreatment required
- Difficult to supply enough biomass to achieve economy of scale

Chemicals:
- Ethanol
- Butanol
- Acetone
- 2,3 Butanediol
- Glycerol
- Acetoin
- Acetic acid
- Lactic acid
- Propionic acid
- Succinic acid
- Butyric acid
- Citric acid
Chemicals: Mixed Acids platform

Lignocellulose → Carboxylic acids/salts → Chemicals

Mixed-Culture Microorganisms

Chemistry

Ketones
Aldehydes
Secondary mixed alcohols
Primary mixed alcohols
Carboxylic acids
Esters
Ethers
Anaerobic Digestion

Biomass

(cellulose, starch,
proteins, fats)

Mixed culture of
microorganisms

Hydrolysis → Acidogenesis → Acetogenesis

(free sugars, amino acids, fatty acids)

(Carboxylic acids, NH₃, CO₂, H₂S)

Carboxylic acids = Volatile fatty acids [VFAs] (e.g., acetic, propionic, butyric, ..., heptanoic acid) (C2 to C7)

Methanogenesis

(Acetic Acid, CO₂, H₂)

(CH₄, CO₂)
Desirable Process Properties

- No sterility
- No GMOs
- Adaptable
- No pure cultures
- Energy in lignin ends up in liquid fuel

- Low capital
- No enzymes
- High product yields
- No vitamin addition
- Co-products not required
Desirable Fuel Properties
# Fuel Properties

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>MTBE</th>
<th>Mixed Alcohols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Volatility</td>
<td>high</td>
<td>low</td>
<td>low</td>
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<tr>
<td>Pipeline shipping</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
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<tr>
<td>Energy content</td>
<td>low</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>high</td>
<td>low</td>
<td>low</td>
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<tr>
<td>Ground water damage</td>
<td>no</td>
<td>yes</td>
<td>no</td>
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</table>
## Properties of Fuel Oxygenates

<table>
<thead>
<tr>
<th>Alcohols</th>
<th>Blending Octane (R + M)/2</th>
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</thead>
<tbody>
<tr>
<td><strong>Vapor Pressure @38°C (kPa)</strong></td>
<td></td>
</tr>
<tr>
<td>Methanol (MeOH)</td>
<td>108</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>115</td>
</tr>
<tr>
<td>Isopropanol (IPA)</td>
<td>106</td>
</tr>
<tr>
<td>tert-Butanol (TBA)</td>
<td>100</td>
</tr>
<tr>
<td>Isobutanol (IBA)</td>
<td>102</td>
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</table>

<table>
<thead>
<tr>
<th>Ethers</th>
<th>Blending Octane (R + M)/2</th>
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<tbody>
<tr>
<td>Methy tertiary butyl ether (MTBE)</td>
<td>110</td>
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<tr>
<td>Di-isopropyl ether (DIPE)</td>
<td>105</td>
</tr>
<tr>
<td>Isopropyl tertiary butyl ether (IPTBE)</td>
<td>113</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy Content</th>
<th>Energy</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MJ/L)</td>
<td>(Btu/gal)</td>
</tr>
<tr>
<td><strong>Gasoline</strong></td>
<td>34.9</td>
<td>125,000</td>
</tr>
<tr>
<td><strong>Mixed Alcohols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Version 1</strong></td>
<td>29.0</td>
<td>104,000</td>
</tr>
<tr>
<td><strong>Mixed Alcohols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Version 2</strong></td>
<td>26.5</td>
<td>95,000</td>
</tr>
<tr>
<td><strong>Ethanol</strong></td>
<td>23.4</td>
<td>84,300</td>
</tr>
</tbody>
</table>
Pretreatment is needed

Source: Michael Ladisch, Purdue Univ.
Lime Treatment

Biomass + Lime

Gravel
In-Situ Digestion

48-h Digestion (g digested/g fed)

- Sugar-cane bagasse
- African millet straw
- Sorghum straw
- Tobacco stalks

- Untreated
- Lime-treated
Lignin Removal

No Air

Air

Lignin Content (g lignin/100 g bagasse)

Time (days)
Mixed-Acid Fermentation

Lime Treatment: 2 weeks, 25°C
Terrestrial Inoculum

Conversion

Total acid concentration (g/L)

LRT (days)

VSLR (g/(L·d))

Air

No Air

Conversion

0 0.2 0.4 0.6 0.8 1

0 10 20 30 40 50 60

18 14 11 8 4 2 20.5 15 10 5 1

0
Building the Pile

~100 ft
Building the Pile
Building the Pile

Crew directing the flow
Fermentation

Biomass → Pretreat → Ferment → Dewater → Thermal Conversion → Hydrogenate

Lime Kiln → Lime → Carboxylate Salts

Calcium Carbonate → Mixed Ketones

Mixed Alcohol Fuels → Hydrogen
Environments where organic acids naturally form

- animal rumen
  - cattle
  - sheep
  - deer
  - elephants
- anaerobic sewage digestors
- swamps
- termite guts
Why are organic acids favored?

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6 & \rightarrow 2 \text{C}_2\text{H}_5\text{OH} + 2 \text{CO}_2 \quad \Delta G = -48.56 \text{ kcal/mol} \\
glucose & \quad \text{ethanol} \\
\text{C}_6\text{H}_{12}\text{O}_6 & \rightarrow 3 \text{C}_2\text{H}_3\text{OOH} \quad \Delta G = -61.8 \text{ kcal/mol} \\
glucose & \quad \text{acetic acid}
\end{align*}
\]

The actual stoichiometry is more complex

\[
\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{acetate} + \text{propionate} + \text{butyrate} + \text{CO}_2 + \text{CH}_4 + \text{H}_2\text{O}
\]
## Typical Product Spectrum at Different Culture Temperatures

<table>
<thead>
<tr>
<th></th>
<th>40°C</th>
<th>55°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2  – Acetic</td>
<td>41 wt %</td>
<td>80 wt %</td>
</tr>
<tr>
<td>C3  – Propionic</td>
<td>15 wt %</td>
<td>4 wt %</td>
</tr>
<tr>
<td>C4  – Butyric</td>
<td>21 wt %</td>
<td>15 wt %</td>
</tr>
<tr>
<td>C5  – Valeric</td>
<td>8 wt %</td>
<td>&lt;1 wt %</td>
</tr>
<tr>
<td>C6  – Caproic</td>
<td>12 wt %</td>
<td>&lt;1 wt %</td>
</tr>
<tr>
<td>C7  – Heptanoic</td>
<td>3 wt %</td>
<td>&lt;1 wt %</td>
</tr>
</tbody>
</table>

100 wt % 100 wt %
Storage + Pretreatment + Fermentation

Biomass + Lime + Calcium Carbonate

Tarp Cover

Gravel

Air
Technology Evolution

- Source of inoculum
- Type of buffer
Marine Inoculum

Air

Terrestrial Inoculum

No Air

Total acid concentration (g/L)

VSLR (g/(L·d))

Conversion

LRT (days)

0 0.2 0.4 0.6 0.8 1
Ammonium Bicarbonate Buffer

40ºC

Graph showing the total acid concentration over time for Ammonium Bicarbonate and Calcium Carbonate.
Ammonium Bicarbonate Buffer

$55^\circ$C

![Graph showing the Total Acid Concentration (g/l) over time with different compounds added at specific time points. The graph includes points for NH$_4$HCO$_3$ and CaCO$_3$.](image-url)
Dewatering

Biomass → Pretreat → Ferment → Dewater → Thermal Conversion

Biomass → Carboxylate Salts

Biomass → Calcium Carbonate

Lime Kiln

Mixed Alcohol Fuels

Mixed Ketones

Hydrogenate

Hydrogen
Vapor-Compression Dewatering

Compressor

Work

Distilled Water

Salt Crystals

Filter

Salt Solution (Fermentor Broth)
Dewatering Energetics

**Ethanol Distillation (5% to 99.9%)**

\[
\frac{\text{kg steam}}{3\text{ L ethanol}} = 8.4 \frac{\text{MJ heat}}{\text{kg ethanol}} = 28.5\% \text{ of the combustion heat}
\]


**MixAlco: Carboxylate Salt Vapor-Compression Dewatering (5% to 100%)**

\[
\frac{54.3 \text{ MJ heat}}{1000 \text{ kg water}} \times \frac{95 \text{ kg water}}{5 \text{ kg acid}} = \frac{1.03 \text{ MJ}}{\text{kg acid}} = 5.9\% \text{ of the combustion heat}
\]

Thermal Conversion

Biomass → Pretreat → Ferment → Dewater → Thermal Conversion

Lime → Lime Kiln

Carboxylate Salts → Calcium Carbonate

Mixed Ketones → Hydrogenate

Mixed Alcohol Fuels → Hydrogen
Thermal Conversion
Stoichiometry

\[ \text{H}_3\text{CCOCaOCCH}_3 \rightarrow \text{H}_3\text{CCCH}_3 + \text{CaCO}_3 \]
Calcium Acetate  Acetone

\[ \text{H}_3\text{CCH}_2\text{COCaOCCH}_2\text{CH}_3 \rightarrow \text{H}_3\text{CCH}_2\text{CCH}_2\text{CH}_3 + \text{CaCO}_3 \]
Calcium Propionate  Diethyl Ketone

\[ \text{H}_3\text{CCH}_2\text{CH}_2\text{COCaOCCH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{H}_3\text{CCH}_2\text{CH}_2\text{CCH}_2\text{CH}_2\text{CH}_3 + \text{CaCO}_3 \]
Calcium Butyrate  Dipropyl Ketone
• Commonly known as dry distillation. Used before and during WWI to make acetone from calcium acetate
Thermal Conversion Kinetics

The graph shows the relationship between temperature ($T$) and time ($t$) for different conversion percentages (99%, 95%, 90%). The conversion increases as the temperature decreases and the time increases.
Hydrogenation

- Pretreat
- Ferment
- Dewater
- Thermal Conversion
- Hydrogenate

- Biomass
- Carboxylate Salts
- Calcium Carbonate
- Mixed Ketones
- Mixed Alcohol Fuels

- Lime Kiln
- Lime

- Hydrogen
Ketone Hydrogenation Stoichiometry

\[
\begin{align*}
\text{Acetone} & \quad \text{Isopropanol} \\
H_3C\text{CCCH}_3 & + H_2 \rightarrow H_3\text{CCH}_3 \\
\text{Methyl Ethyl Ketone} & \quad \text{2-Butanol} \\
H_3\text{CCH}_2\text{CH}_3 & + H_2 \rightarrow H_3\text{CCH}_2\text{CH}_3 \\
\text{Diethyl Ketone} & \quad \text{3-Pentanol} \\
H_3\text{CCH}_2\text{CCH}_2\text{CH}_3 & + H_2 \rightarrow H_3\text{CCH}_2\text{CCH}_2\text{CH}_3
\end{align*}
\]
Ketone Hydrogenation

Catalyst = 200 g/L Raney nickel
Temperature = 130°C
Time = 35 min
@ P = 15 atm (220 psi)
Hydrogenation

Ketone → Alcohol → Steam

Hydrogen
MixAlco Process – Version 2

Biomass → Pretreat → Ferment → Dewater → Acid Springing → Esterification → Hydrogenolysis

Mixed Alcohol Fuels

Hydrogen

Lime Kiln → Lime → Carboxylate Salts

Calcium Carbonate → Mixed Acids
Acid “Springing” Calcium Salts

Ca(Ac)$_2$ + H$_2$O → CO$_2$ + CaCO$_3$ + R$_3$NHAc

R = - CH$_2$CH$_3$

R = - CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
Acid “Springing” Ammonium Salts

\[ \text{R} = -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]
MixAlco Process – Version 2

Biomass → Pretreat → Ferment → Dewater → Acid Springing → Esterification → Hydrogenolysis

- Lime Kiln
- Calcium Carbonate
- Carboxylate Salts
- Mixed Acids
- Mixed Alcohol Fuels
- Hydrogen
Hydrogenation Stoichiometry

\[
\begin{align*}
\text{O} & \quad \text{H}_3\text{CCOOH} + \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \rightarrow & \quad \text{H}_3\text{CCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \\
\text{Heavy Alcohol} & & & \text{Ester} \\
\text{O} & \quad \text{H}_3\text{CCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + 2 \text{H}_2 & \rightarrow & \quad \text{H}_3\text{CCOOH} + \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{Ester} & & & \text{Heavy Alcohol} \\
\text{H}_3\text{CCOOH} + 2 \text{H}_2 & \rightarrow & \quad \text{H}_3\text{CCOOH} + \text{H}_2\text{O} \\
\text{Acetic Acid} & & & \text{Ethanol}
\end{align*}
\]
Esterification + Hydrogenolysis

Water → Esters → Alcohols

Mixed Alcohols → Heavy Alcohols

Carboxylic Acids

H₂
Esterification + Hydrogenolysis

Water + NH$_3$ → Mixed Alcohols

NH$_4$ Carboxylate Salts → Esters → Alcohols → Heavy Alcohols → H$_2$
Esterification

• Acid catalyzed \((H_2SO_4)\) or solids acid catalysts. Same reaction as free fatty acids esterification in biodiesel production.
Ester Hydrogenolysis

- Copper chromite
  - high temperatures (> 200°C)
  - high pressures (> 600 psi)
  - 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)
  - preferred
## Plant Capacity

<table>
<thead>
<tr>
<th>Plant Capacity</th>
<th>(tonne/h)</th>
<th>(mill gal/yr)</th>
<th>*City Population</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Version 1</td>
<td>Version 2</td>
<td></td>
</tr>
<tr>
<td>Base Case</td>
<td>2</td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.6</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>30.3</td>
<td>45.1</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>121</td>
<td>181</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>606</td>
<td>903</td>
</tr>
</tbody>
</table>

* Feedstock = Municipal solid waste + Sewage sludge
Effect of Scale on Capital Cost – Versions 1 & 2

![Graph showing the effect of scale on capital cost. The x-axis represents capacity in tonnes per hour, ranging from 0 to 900, and the y-axis represents capital cost in million dollars, ranging from 0 to 300. The graph shows a linear relationship between capacity and capital cost.]
## Mixed Secondary Alcohols (e.g., isopropanol) (Version 1)

<table>
<thead>
<tr>
<th>Biomass Feed Capacity (tonne/h)†</th>
<th>Alcohol Prod'n (million gal/yr)</th>
<th>Estimated Capital Cost*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.5</td>
<td>$2.65 million</td>
</tr>
<tr>
<td>10</td>
<td>7.6</td>
<td>$7.77 million</td>
</tr>
<tr>
<td>40</td>
<td>30.3</td>
<td>$19.7 million</td>
</tr>
<tr>
<td>160</td>
<td>121</td>
<td>$66.3 million</td>
</tr>
<tr>
<td>800</td>
<td>606</td>
<td>$287 million</td>
</tr>
</tbody>
</table>

Yield = ~ 86 gal/dry ton
Mixed Acid Selling Price
Version 2 (15% ROI)

Biomass Cost ($/tonne)

Capacity (tonne/h)

Acid Selling Price ($/lb)
## Carboxylic Acids

<table>
<thead>
<tr>
<th>Biomass Feed Capacity (tonne/h)</th>
<th>Mixed Acid Prod'n (million lb/yr)</th>
<th>Estimated Capital Cost*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>18.3</td>
<td>$2.49 million</td>
</tr>
<tr>
<td>10</td>
<td>91.5</td>
<td>$7.31 million</td>
</tr>
<tr>
<td>40</td>
<td>366</td>
<td>$18.6 million</td>
</tr>
<tr>
<td>160</td>
<td>1,460</td>
<td>$63.6 million</td>
</tr>
<tr>
<td>800</td>
<td>7,320</td>
<td>$280 million</td>
</tr>
</tbody>
</table>
Mixed Alcohol Selling Price
Version 2
(15% ROI)
Mixed Primary Alcohols (e.g., ethanol) (Version 2)

<table>
<thead>
<tr>
<th>Primary Alcohols</th>
<th>Biomass Feed Capacity (tonne/h)†</th>
<th>Alcohol Prod'n (million gal/yr)</th>
<th>Estimated Capital Cost*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>2.25</td>
<td>$2.65 million</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>11.3</td>
<td>$7.77 million</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>45.1</td>
<td>$19.7 million</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>181</td>
<td>$66.3 million</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>903</td>
<td>$287 million</td>
</tr>
</tbody>
</table>

Yield = ~ 130 gal/dry ton
Yield = ~100 gal/dry ton for bagasse
(90% of theoretical)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Theoretical Yield in gallons per dry ton of feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Grain</td>
<td>124.4</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>113.0</td>
</tr>
<tr>
<td>Rice Straw</td>
<td>109.9</td>
</tr>
<tr>
<td>Cotton Gin Trash</td>
<td>56.8</td>
</tr>
<tr>
<td>Forest Thinnings</td>
<td>81.5</td>
</tr>
<tr>
<td>Hardwood Sawdust</td>
<td>100.8</td>
</tr>
<tr>
<td>Bagasse</td>
<td>111.5</td>
</tr>
<tr>
<td>Mixed Paper</td>
<td>116.2</td>
</tr>
</tbody>
</table>

Source: http://www1.eere.energy.gov/biomass/ethanol_yield_calculator.html
## Energy Content

<table>
<thead>
<tr>
<th></th>
<th>Energy</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MJ/L)</td>
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<tr>
<td>Gasoline</td>
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</tr>
<tr>
<td>Mixed Alcohols</td>
<td>29.0</td>
<td>104,000</td>
</tr>
<tr>
<td>Version 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed Alcohols</td>
<td>26.5</td>
<td>95,000</td>
</tr>
<tr>
<td>Version 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>23.4</td>
<td>84,300</td>
</tr>
</tbody>
</table>
Yield on an ethanol equivalent basis

\[
130 \text{ gal/ton} \times \frac{95,000}{84,300} = 147 \text{ gal/ton}
\]

\(~50\%\) more than enzymatic/ethanol fermentation route
Conclusions

• The technology is
  - “green”
  - profitable
  - world-wide
  - simple
• Many potential products
  - ketones
  - alcohols
  - organic acids
Conclusions

- **Near-term applications**
  - waste $\rightarrow$ chemicals
- **Mid-term applications**
  - waste $\rightarrow$ fuels
- **Far-term applications**
  - crops $\rightarrow$ fuels
Thank you for your time and attention