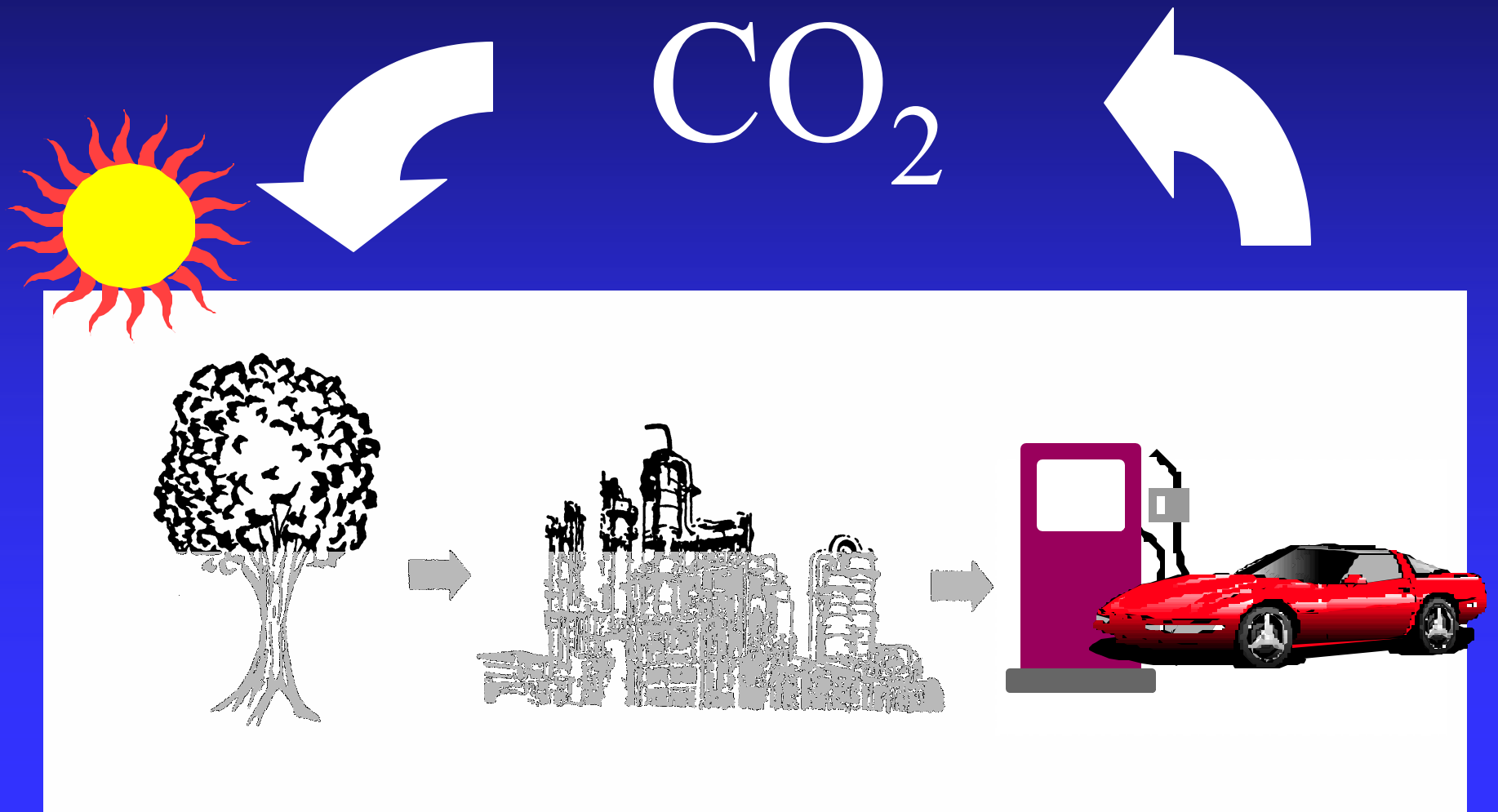


# **MixAlco: Biofuels from Biomass**

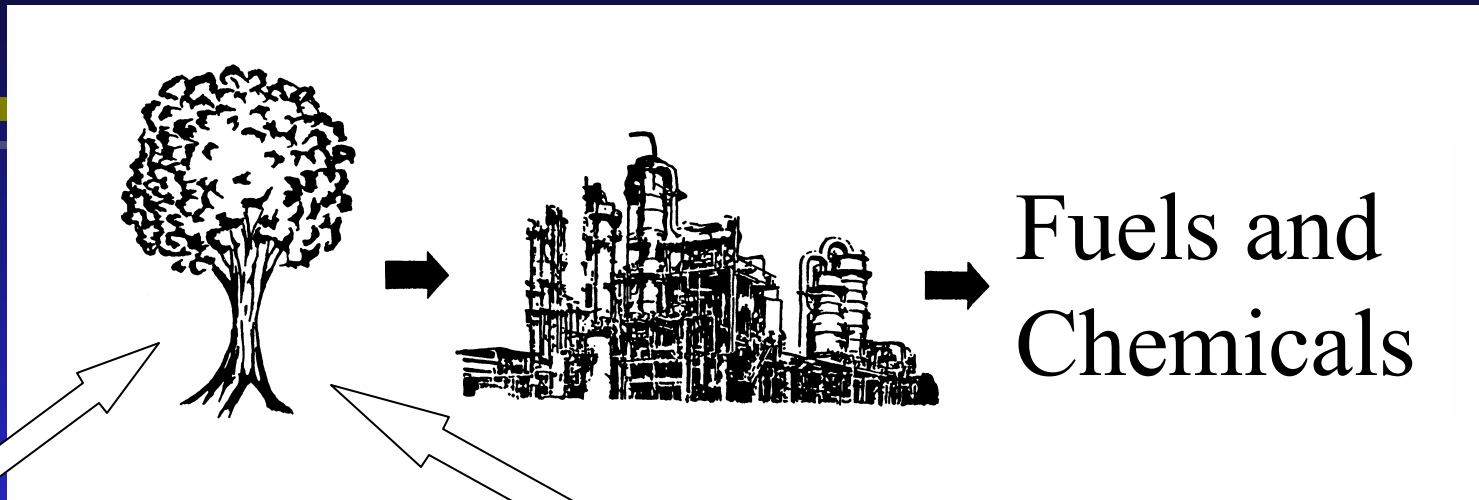
**Professor Mark Holtzapple  
Department of Chemical Engineering  
Texas A&M University**

Presentation by  
Scott L. Wellington, PhD  
Research Advisor  
Shell International E&P

# Biofuels



# Examples of Biomass



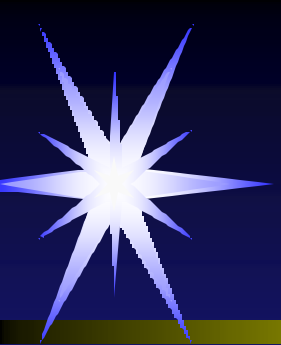
- forest residues & trees
- grass clippings
- agricultural residues
- energy crops
- municipal solid waste
- sewage sludge
- animal manure

most of these are “lignocellulose.”

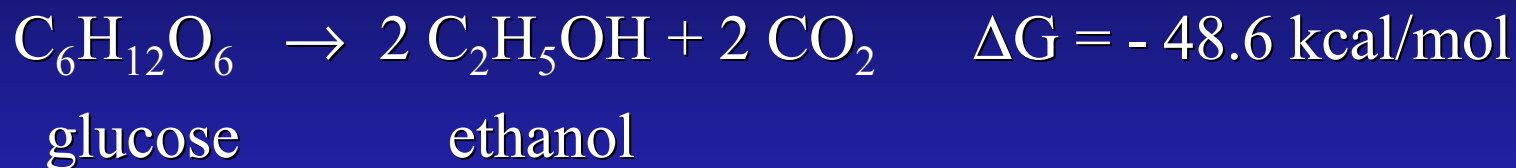


# Nature Converts “Cellulose” into Organic Acids, i.e.,

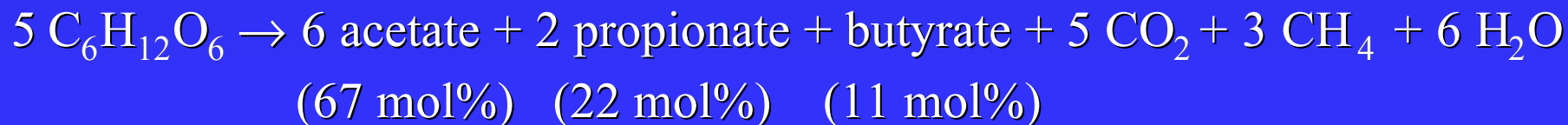
- animal rumen
  - cattle
  - sheep
  - deer
  - elephants
- anaerobic sewage digestors
- swamps
- termite guts



# Why are Organic Acids Favored?



The actual stoichiometry is complex: Briefly



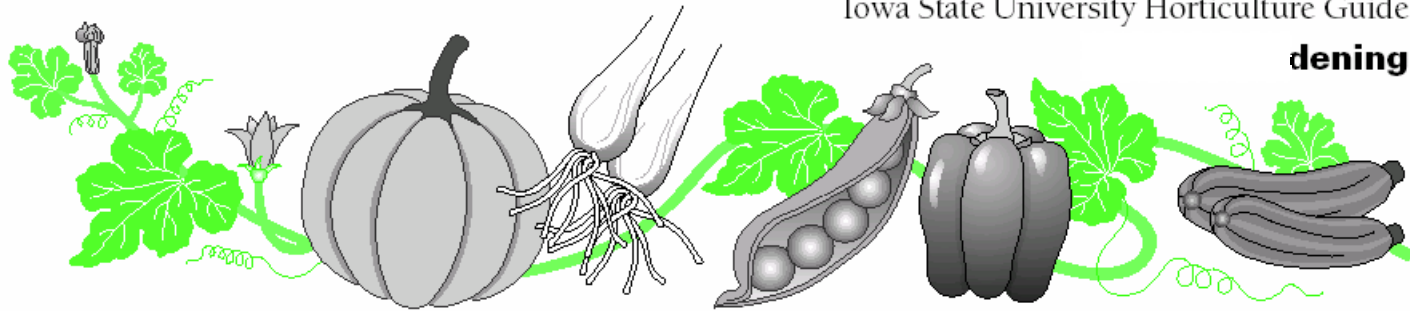
# Conversion of City Yard, Crop and Forreast Waste



Composting

Iowa State University Horticulture Guide

**dening**

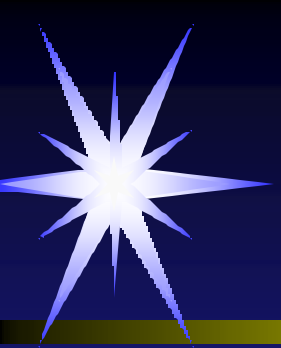




# Research Statistics

- Year started = early 1991
- Time spent = 13 years
- Labor =  $\sim 110$  person·years
- Funding, over \$2.3 mill





# Researchers

## Faculty

- **Mark Holtzapple**
- Richard Davison

## Post Docs

- Praveen Vadlani
- Vincent Chang
- Xu Li
- Cesar Granda

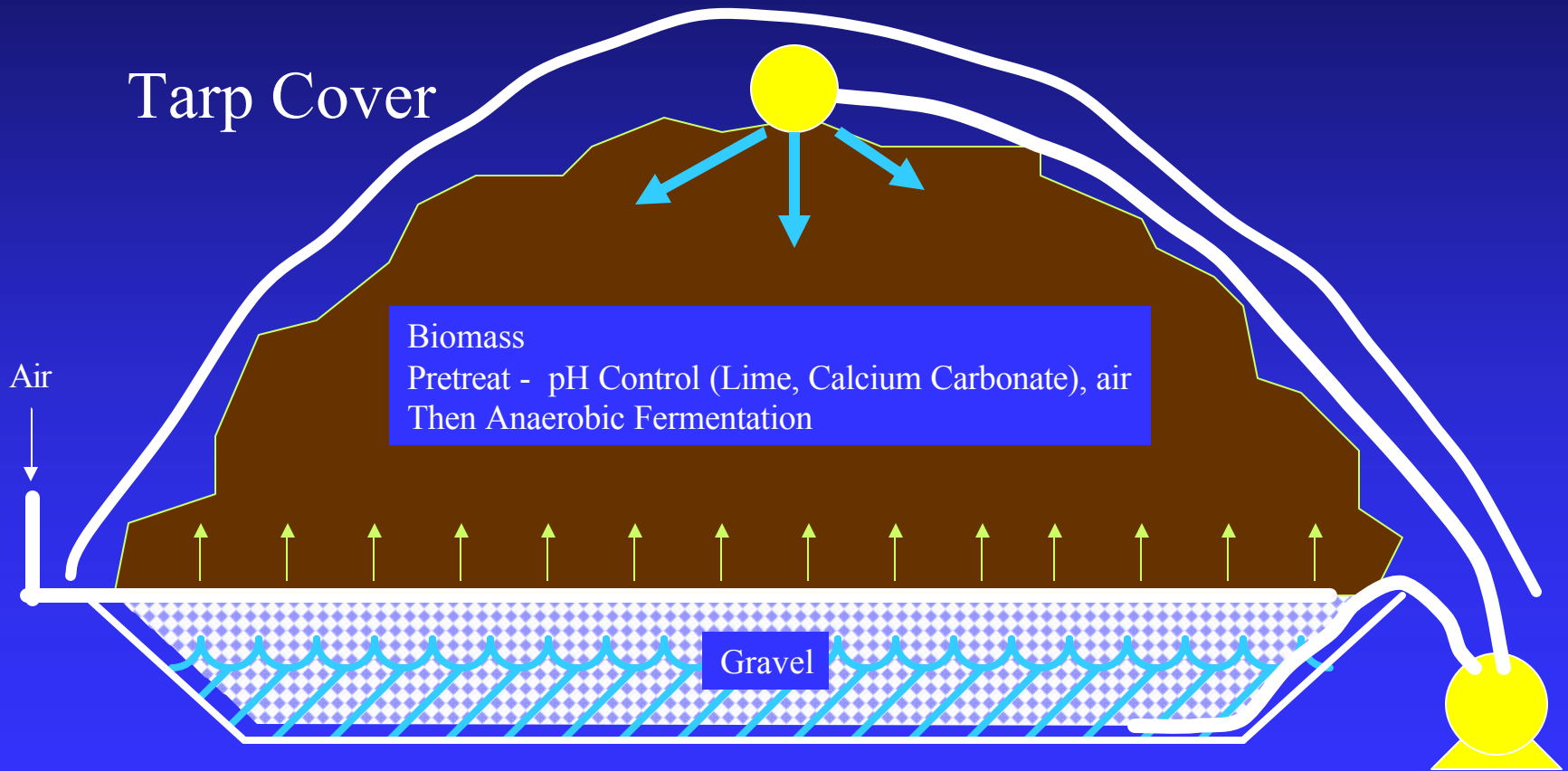
## Masters

- Murlidhar Nagwani
- Chang Ming Lee
- Champion Lee
- Seth Adleson
- Robert Rapier
- William Kaar
- David Gaskin
- Hiroshi Shirage
- Wilbelto Adorno-Gomez
- Shelly Williamson
- Maria Almendarez
- Ramasubramania Narayan
- Patricia O'Dowd
- Hung-Wen Yeh
- Manohar Vishwanathappa

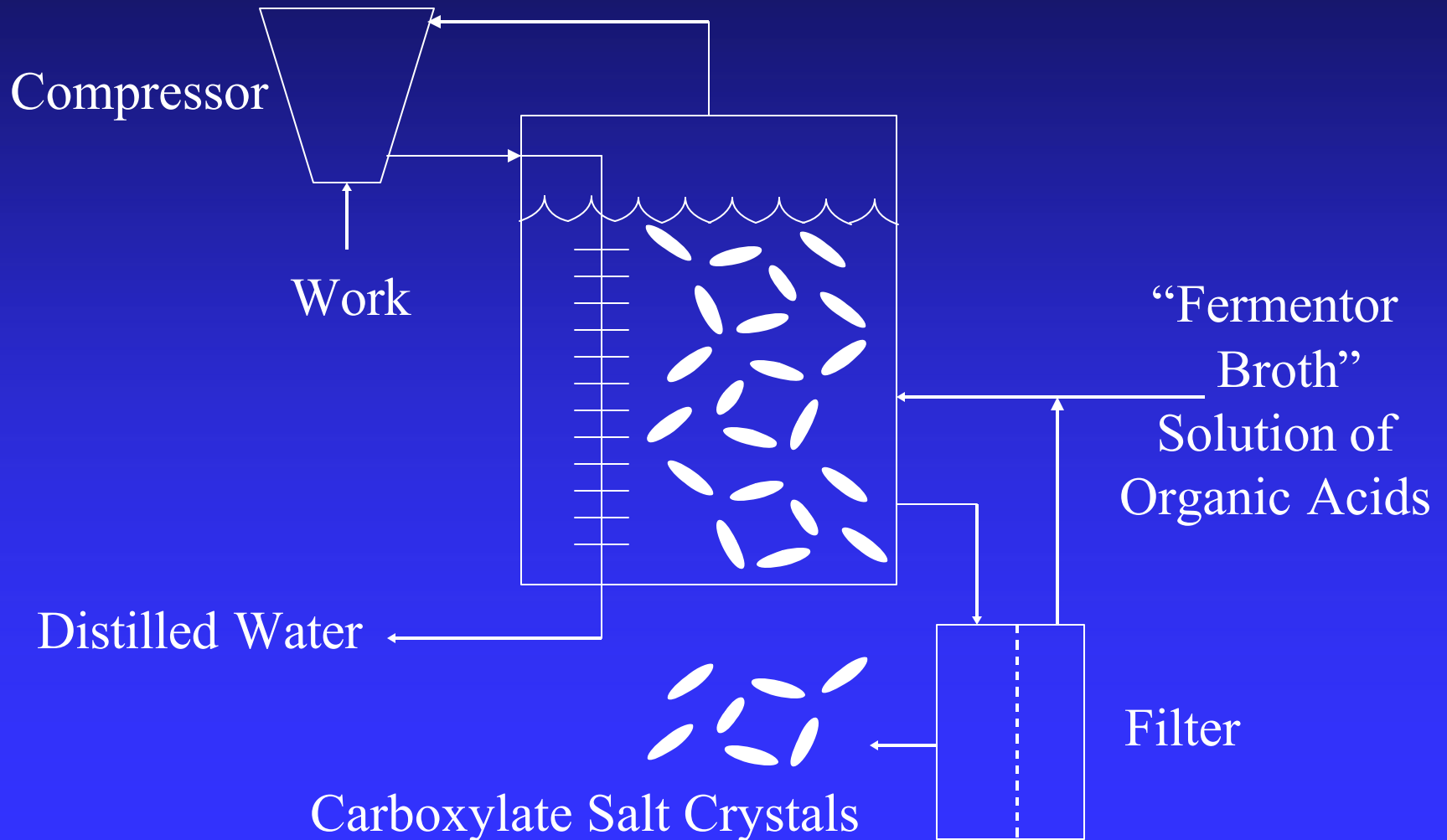
## PhD

- Nan Sheng Chang
- Shushien Chang
- Mitch Loescher
- Kyle Ross
- Susan Domke
- Salvador Aldrett-Lee
- Cateryna Aiello-Mazzarri
- Wenning Chan
- Piyarat Thanakoses
- Xu Li
- Guillermo Coward-Kelly
- Li Zhu
- Se Hoon Kim
- Frank Agbogbo
- Zihong Fu
- Jonathan O'Dwyer

# Aerobic Compost Pretreatment then Anaerobic Fermentation

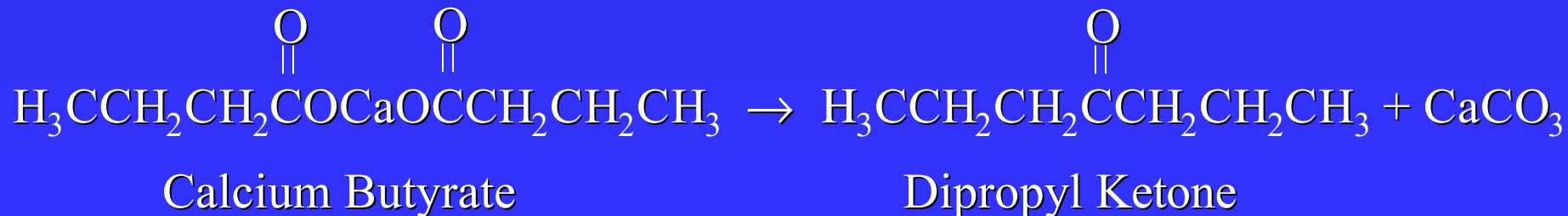
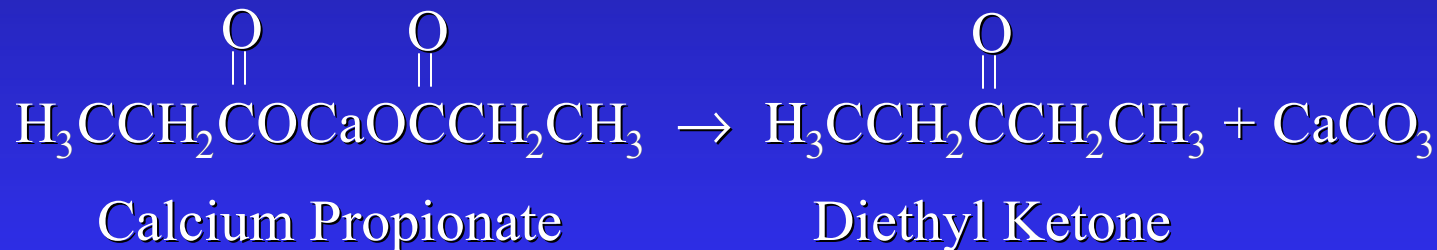
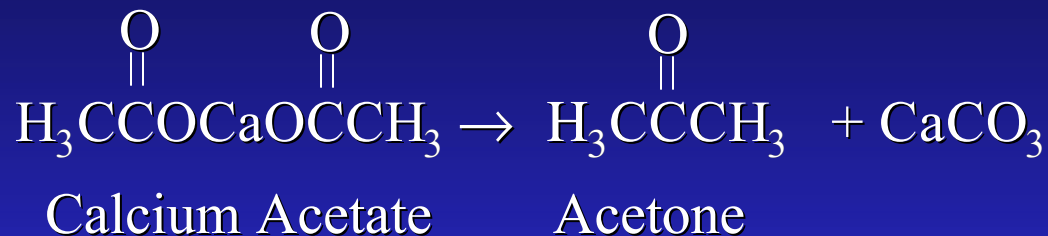


# Vapor-Compression Dewatering

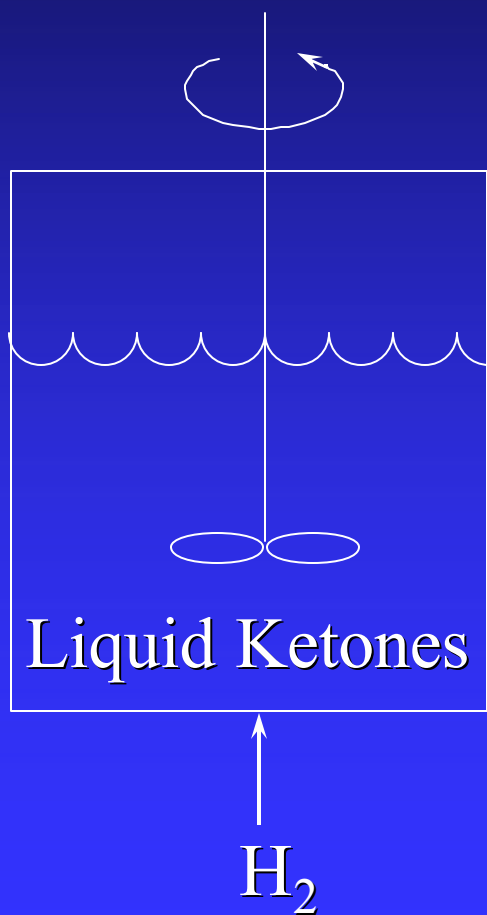




# Thermal Conversion Stoichiometry (One Option)



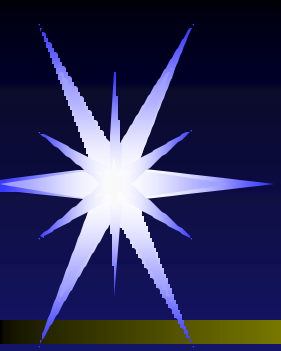
# Ketone Hydrogenation Option



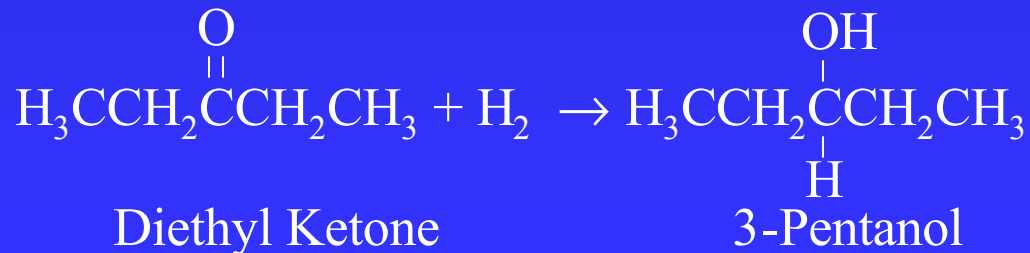
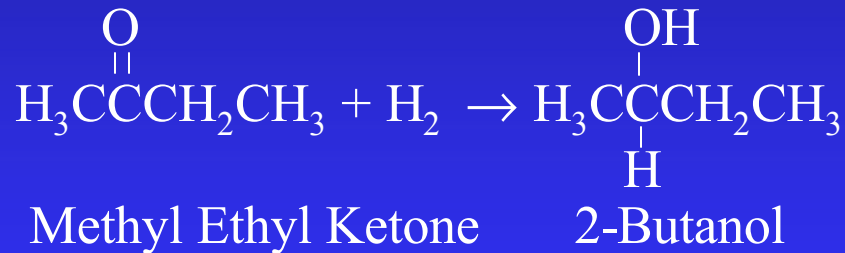
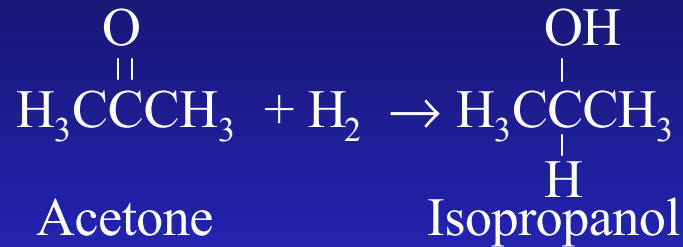
Catalyst = 200 g/L Raney nickel

Temperature = 130°C

Time = 35 min (@ P = 15 atm)



# Ketone Hydrogenation Stoichiometry



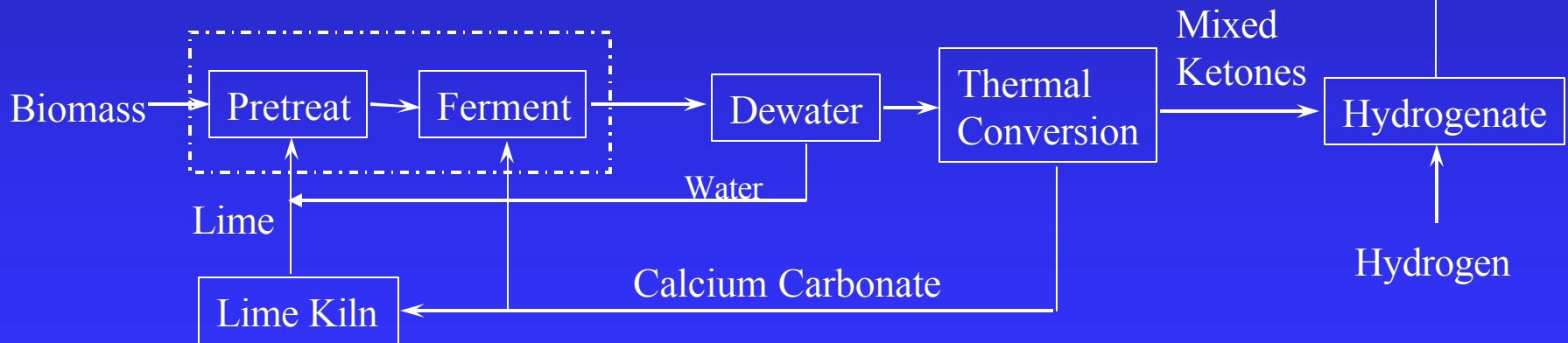
# MixAlco Process:

**1) Compost  
Pretreatment  
&  
Fermentation**

**2) Dewater  
&  
Collect  
Carboxylate  
Salts**

**3) Heat to  
Form Ketones:  
Many Process  
Options and  
Products**

**4) Hydrotreat  
to Alcohols**





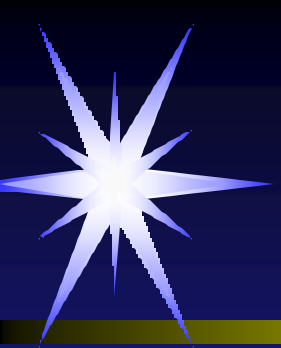
# Typical Product Spectrum at Different Fermentation Temperatures

	40°C	55°C
C2 – Acetic	41 wt %	80 wt %
C3 – Propionic	15 wt %	4 wt %
C4 – Butyric	21 wt %	15 wt %
C5 – Valeric	8 wt %	<1 wt %
C6 – Caproic	12 wt %	<1 wt %
C7 – Heptanoic	<u>3 wt %</u>	<u>&lt;1 wt %</u>
	100 wt %	100 wt %



# Energy Content

	Energy	
	(MJ/L)	(Btu/gal)
Gasoline	34.9	125,000
Mixed Alcohols	29.0	104,000
Ethanol	23.4	84,300



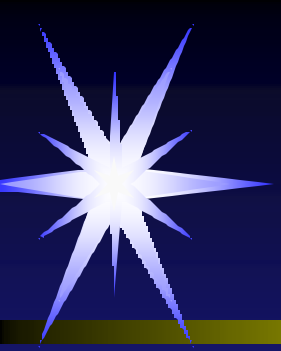
# Properties of Fuel Oxygenates

Blending Reid  
Vapor Pressure  
@38°C (kPa)

Blending  
Octane  
(R + M)/2

## Alcohols

214	Methanol (MeOH)	108
124	Ethanol (EtOH)	115
97	Isopropanol (IPA)	106
62	<i>tert</i> -Butanol (TBA)	100
34	Isobutanol (IBA)	102



# Key Numbers

$$\text{Conversion} = 0.75 \frac{\text{tonne digested}}{\text{tonne fed}}$$

$$\text{Selectivity} = 0.65 \frac{\text{tonne acids}}{\text{tonne fed}}$$

$$\text{Yield} = 0.75 \frac{\text{tonne digested}}{\text{tonne fed}} \times 0.65 \frac{\text{tonne acids}}{\text{tonne digested}} = 0.49 \frac{\text{tonne acids}}{\text{tonne fed}}$$

Solid residue will be burned for process heat, sold as compost, or landfilled.



# U.S. Biodegradable Wastes

Wastes Only	Amount (million tonne/year)	Alcohol Potential (billion gal/year)
Municipal Solid Waste	78	10
Sewage Sludge	10.9	1.4
Industrial Biosludge	3	0.4
Recycled Paper Fines	4.3	0.5
Agricultural Residues	400	52
Forestry Residues	330	43
Manure	220	28
Total	1,046	135

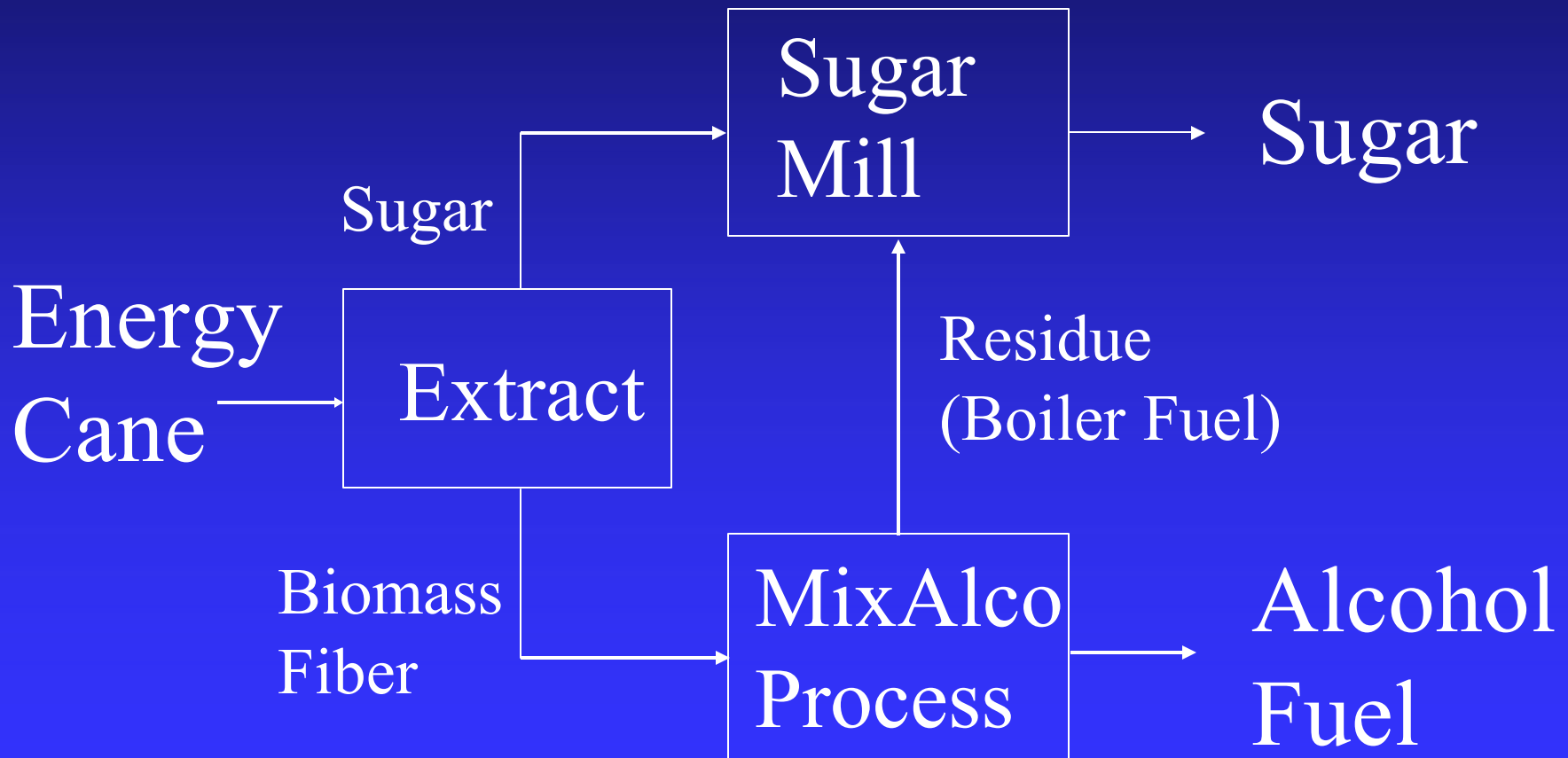
U.S. Gasoline Consumption = 130 billion gal/year

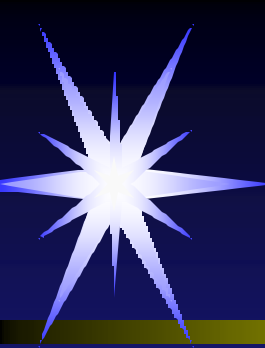
U.S. Diesel Consumption = 40 billion gal/year

# Fuels and Sugar from Energy Cane



# Energy Cane Processing





# Sweet Sorghum

Grows in ~35 US states

Yield = 20–25 dry ton/(acre·yr)



345 mi



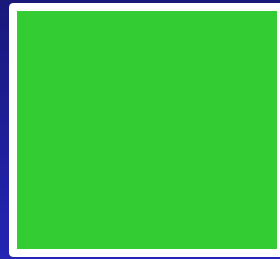
William Rooney, Soil and Crop Sciences, Texas A&M University

# Land Area in United States



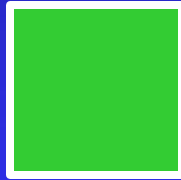
# Effect of Automotive Efficiency

1×  
(Current)



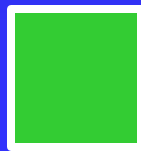
302 mi

2× better



213 mi

3× better



174 mi



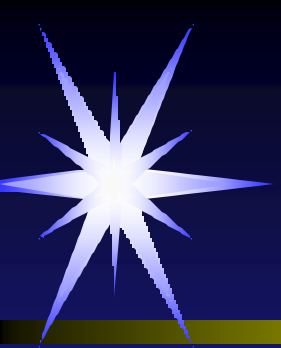


# U.S. Biodegradable Wastes

Wastes Only	Amount (million tonne/year)	Alcohol Potential (billion gal/year)
Municipal Solid Waste	78	10
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Forestry Residues	330	43
Manure	220	28
Total	1,046	135

U.S. Gasoline Consumption = 130 billion gal/year

U.S. Diesel Consumption = 40 billion gal/year



# Advantages of MixAlco Approach

- robust efficient nonsterile fermentation
- natural occurring microorganisms
- culture passed from one compost pile to another
- no spoiled batches since natural process
- inexpensive compost like pretreat & fermentation
- no enzyme addition required
- conventional plant operation and fuel distribution
- flexible using organic residue wastes and/or crops
- high performance bio-fuel or fuel additive products



The MixAlco Process is: - “green” - simple  
- robust - widely applicable and - timely

**Professor Holtapple  
is the Recipient of  
the Presidential  
Green Chemistry  
Award**





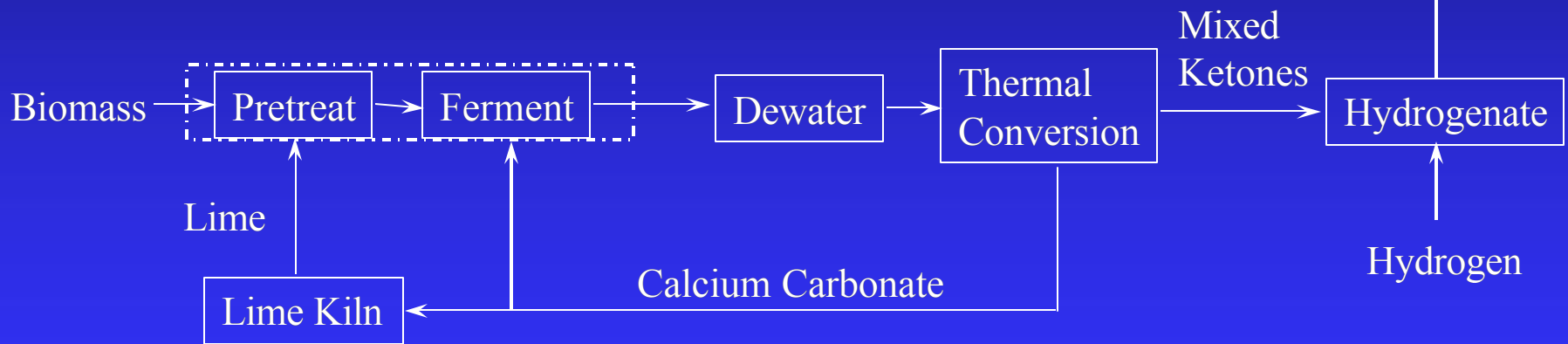
# MixAlco Process Next Steps

- ✓ **Convert Pilot Plant for Other Studies**
  - 3 Quarter 2005
- ✓ **Complete Design of Demonstration Plant**
  - Year End 2004
- ✓ **Organize a Demonstration Project**
  - Early 2004
- ✓ **Commercialize the Process**
  - ASAP

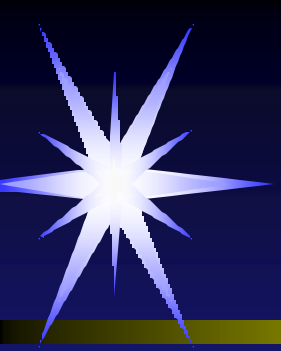
# Patents

5,865,898 5,962,307  
5,693,296 5,874,263

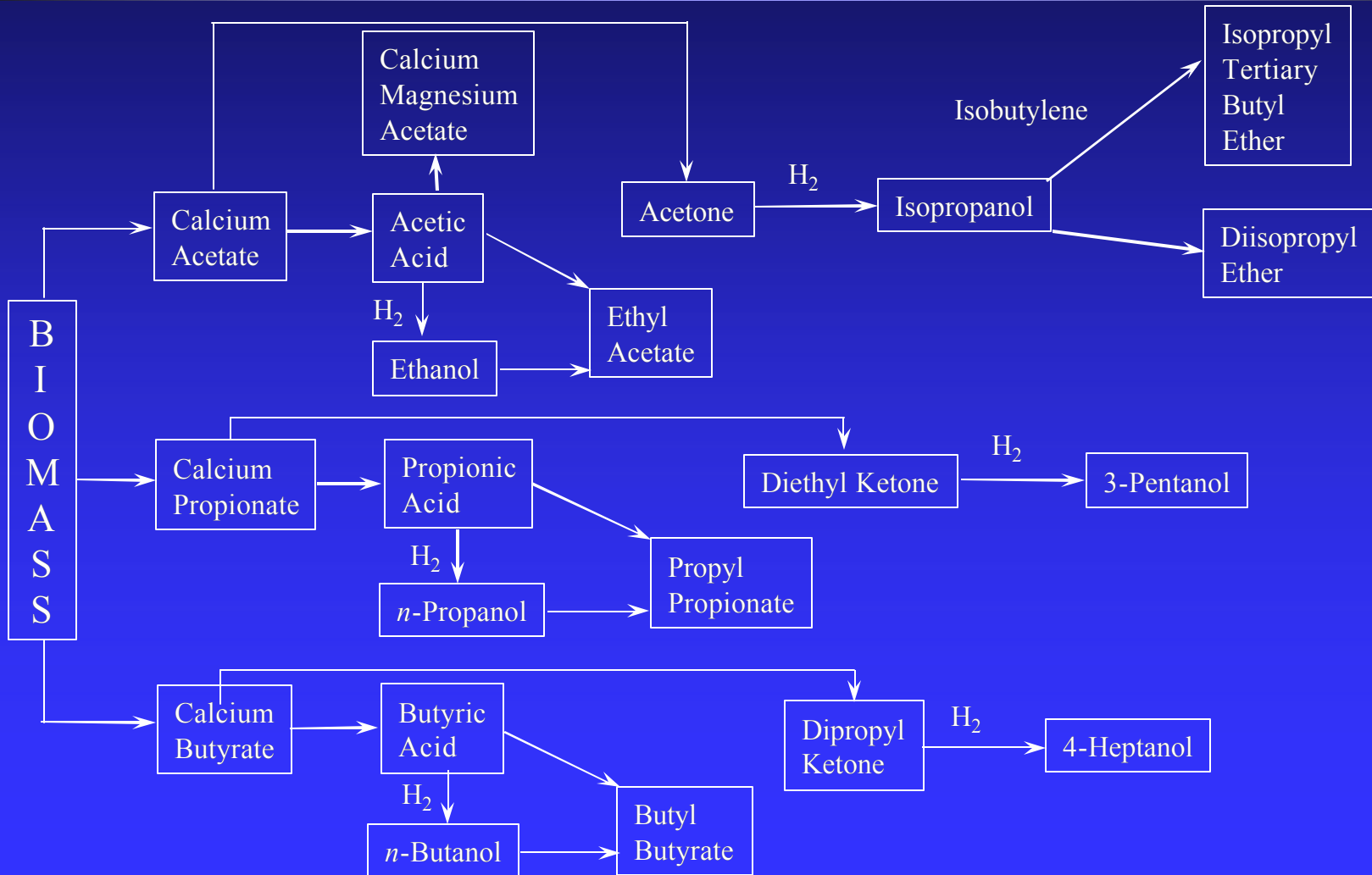
5,969,189  
5,986,133 6,262,313



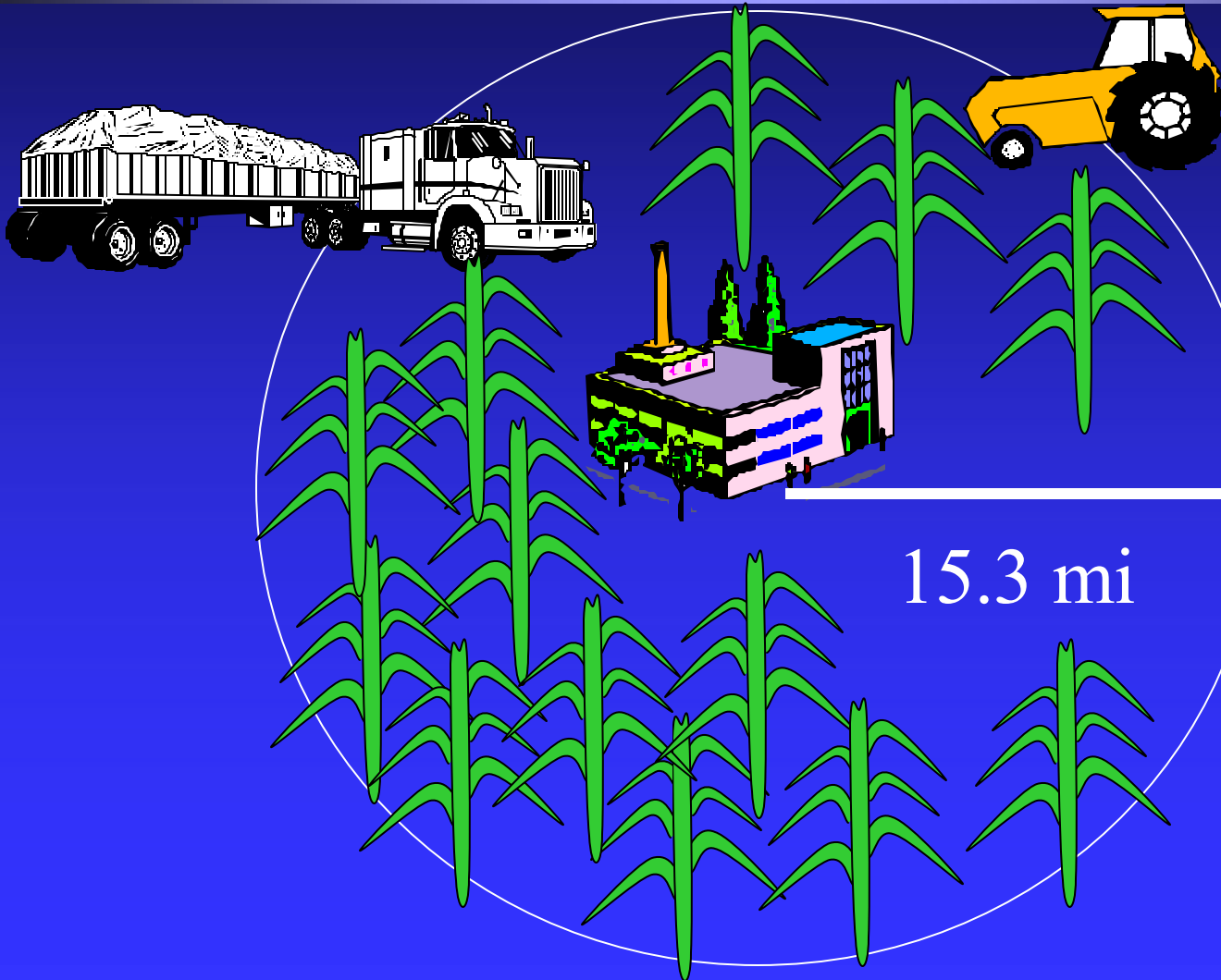
6,043,392  
6,395,926



# Chemical Flowchart



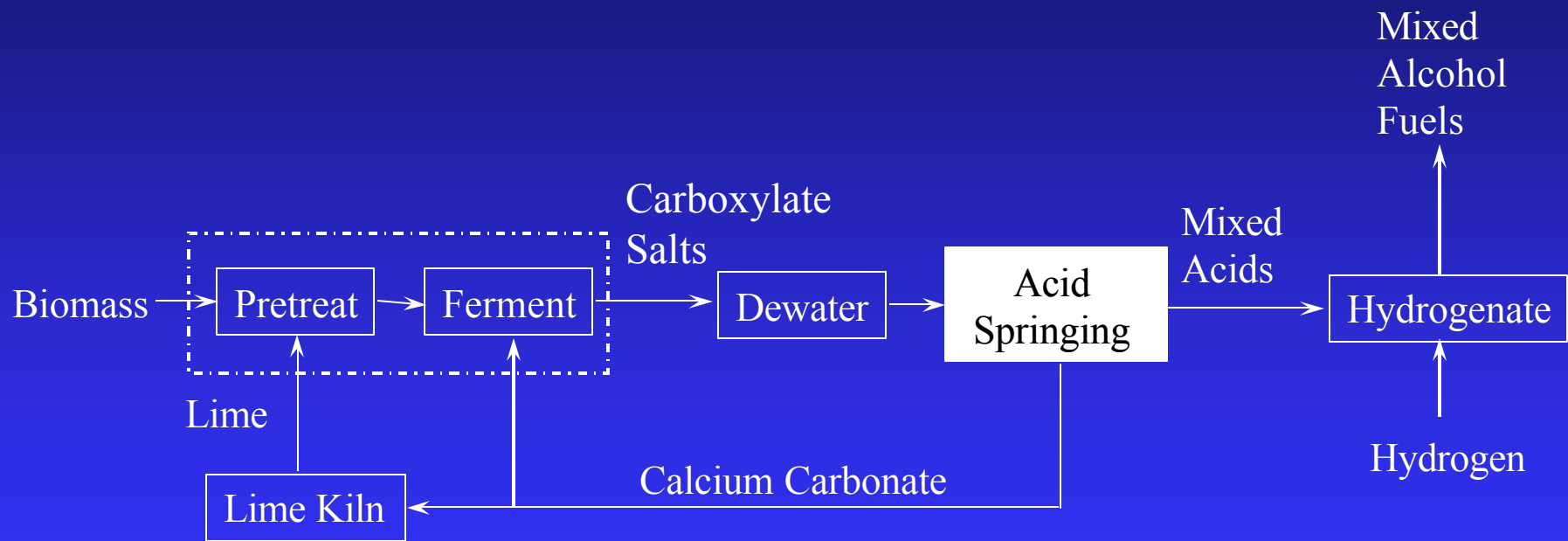
# Centralized Processing



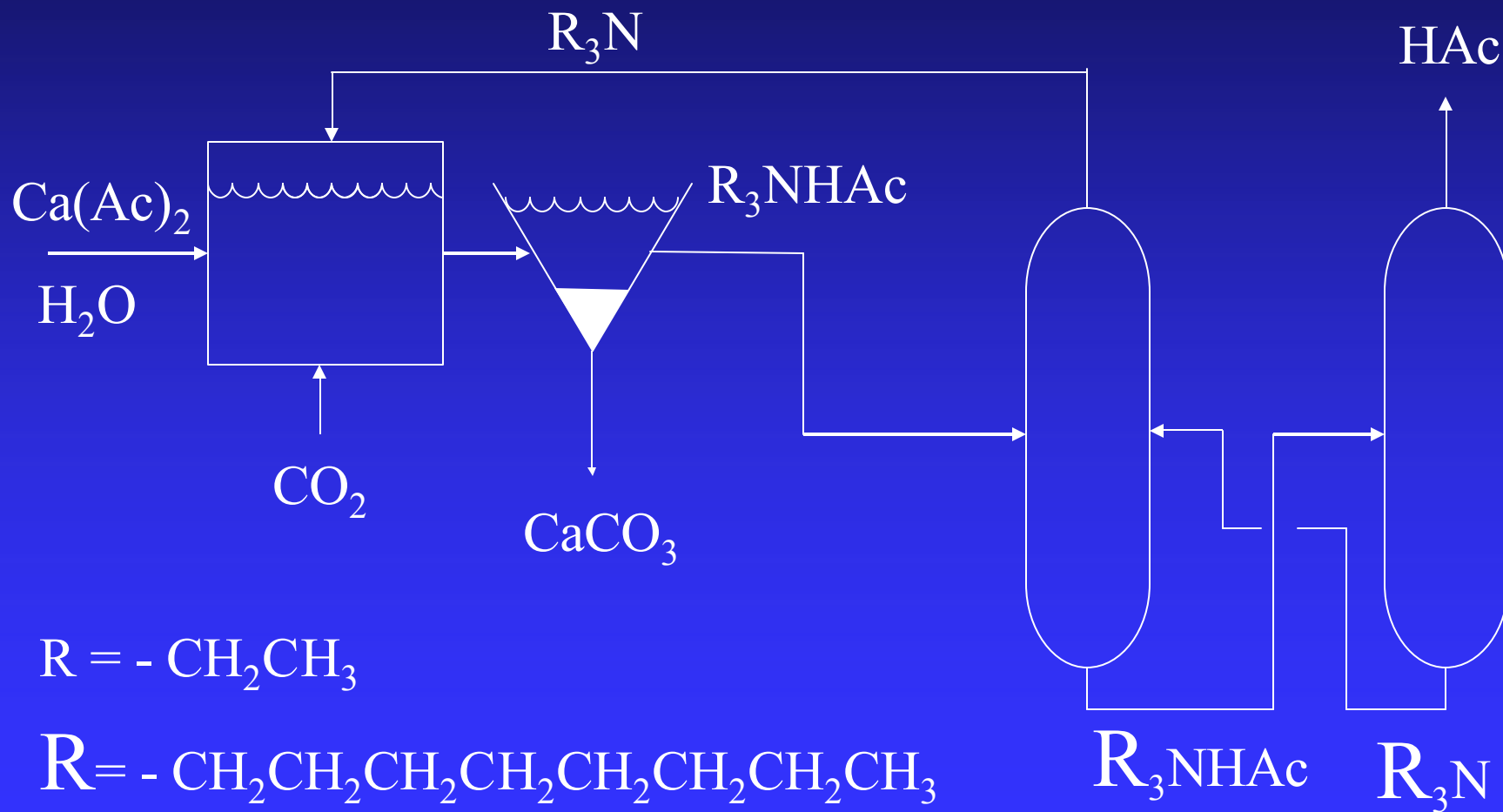
15.3 mi

50% of area  
planted

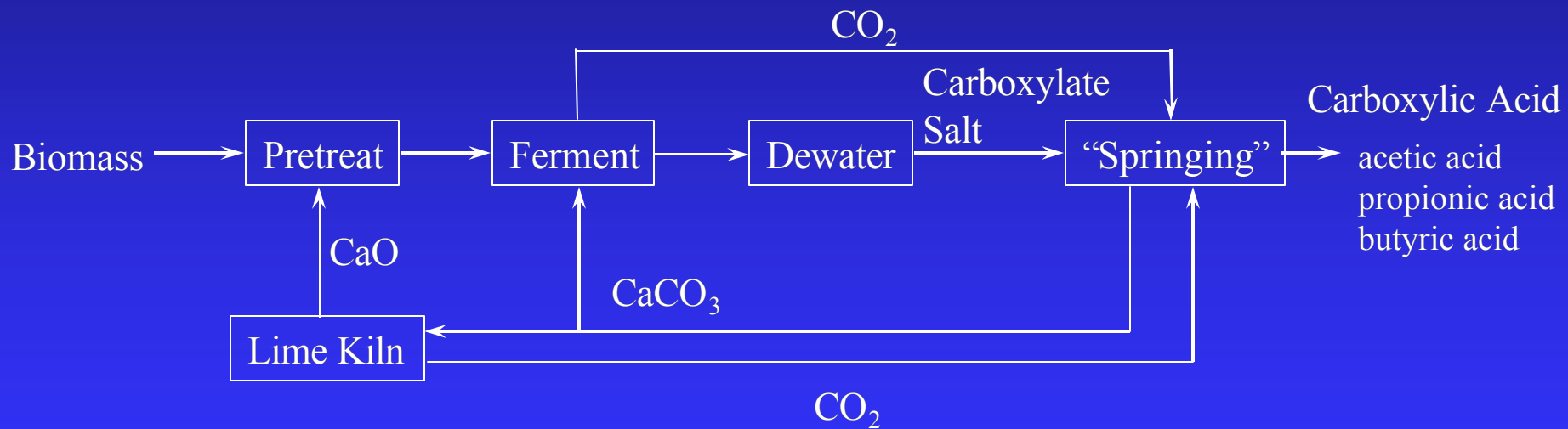
# MixAlco Process – Version 2



# Acid "Springing"



# Carboxylic Acid Production









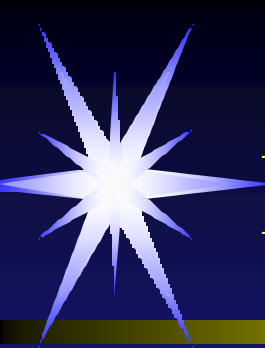


# Required Area

Scale = 800 tonne/h

Feedstock yield = 30 ton/(acre·yr)

$$\begin{aligned} \text{Area} &= \frac{800 \text{ tonne}}{\text{h}} \times \frac{8000 \text{ h}}{\text{yr}} \times \frac{1.1 \text{ ton}}{\text{tonne}} \times \frac{\text{acre}\cdot\text{yr}}{30} = 235,000 \text{ acre} \\ &= 366 \text{ mi}^2 \end{aligned}$$



# Feedstock

## Yard Clippings

$$\frac{1000 \text{ wet ton}}{\text{d}} \times \frac{0.5 \text{ dry ton}}{\text{wet ton}} \times \frac{\text{tonne}}{1.1 \text{ ton}} \times \frac{280 \text{ d}}{\text{yr}} \times \frac{\text{yr}}{8000 \text{ h}} = 16 \frac{\text{dry tonne}}{\text{h}}$$

## Sewage Sludge

$$\frac{650 \text{ wet ton}}{\text{d}} \times \frac{0.3 \text{ dry ton}}{\text{wet ton}} \times \frac{\text{tonne}}{1.1 \text{ ton}} \times \frac{365 \text{ d}}{\text{yr}} \times \frac{\text{yr}}{8000 \text{ h}} = 8 \frac{\text{dry tonne}}{\text{h}}$$

$$\text{Total} = 24 \frac{\text{tonne}}{\text{h}}$$



# Key Assumptions

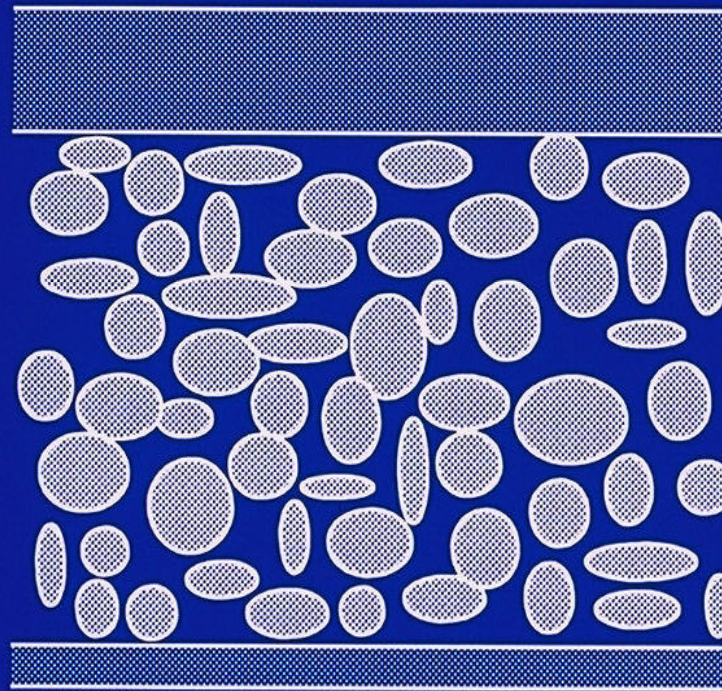
$$\text{Conversion} = 0.83 \frac{\text{tonne digested}}{\text{tonne fed}} \quad (\text{High because of sugar})$$

$$\text{Selectivity} = 0.65 \frac{\text{tonne acids}}{\text{tonne fed}}$$

$$\text{Yield} = 0.83 \frac{\text{tonne digested}}{\text{tonne fed}} \times 0.65 \frac{\text{tonne acids}}{\text{tonne digested}} = 0.54 \frac{\text{tonne acids}}{\text{tonne fed}}$$

$$\text{Product} = \frac{0.54 \text{ tonne acids}}{\text{tonne fed}} \times \frac{0.54 \text{ tonne alcohol}}{\text{tonne acids}} = 0.29 \frac{\text{tonne alcohols}}{\text{tonne fed}}$$

# Fermentor Liner



Abrasion-Resistant  
Liner

Gravel

Geomembrane



# Production Rate

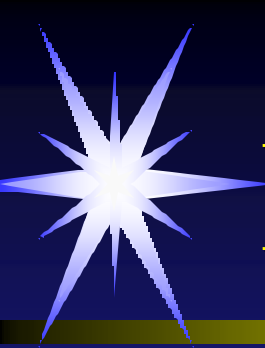
$$\text{Production Rate} = \frac{800 \text{ tonne fed}}{\text{h}} \times \frac{0.29 \text{ tonne alcohols}}{\text{tonne fed}} = 233 \frac{\text{tonne alcohols}}{\text{h}}$$

$$= 297,000 \text{ L/h}$$

$$= 78,600 \text{ gal/h}$$

$$= 44,900 \text{ bbl/d}$$

$$= 629 \text{ mill gal/yr}$$



# Plant Capacity

		Plant Capacity		City Population
		(tonne/h)	(mill gal/yr)	
Base Case →		2	1.1	40,000
		10	5.6	200,000
		40	22.3	800,000
		160	89.3	3,200,000
		800	446.7	16,000,000

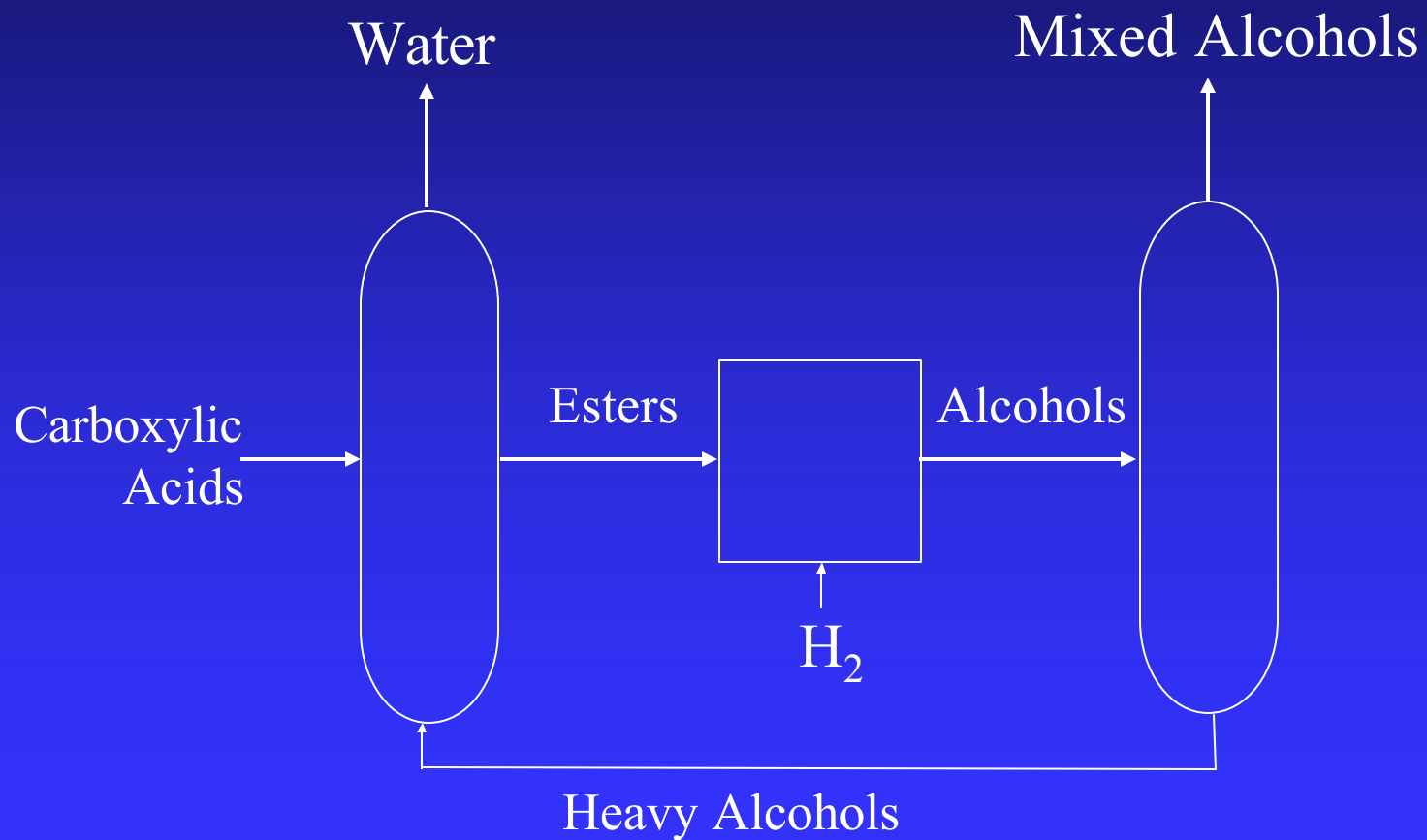


# What is lignocellulose?

---

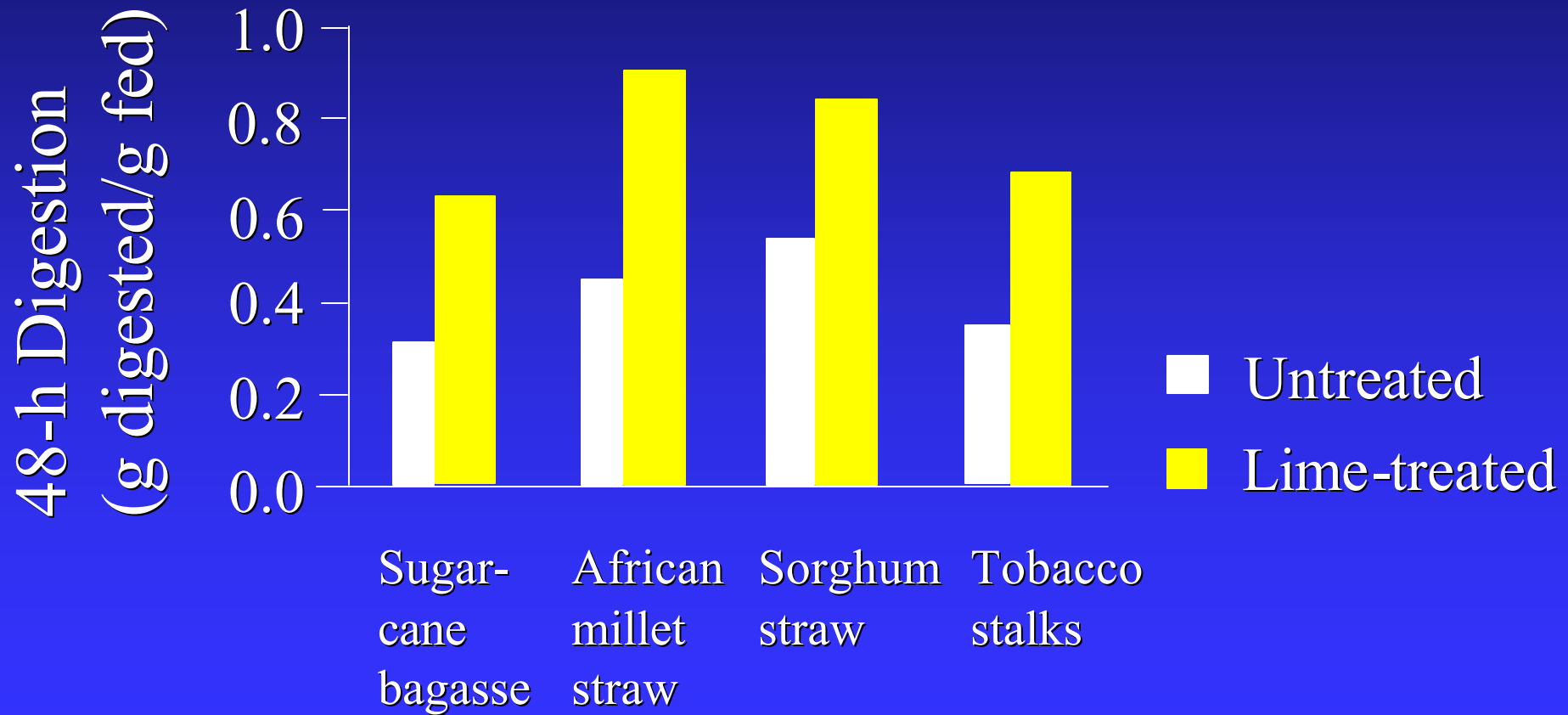
- Cellulose - glucose polymer
- Hemicellulose - xylose polymer
- Lignin - aromatic polymer

# Hydrogenation





# *In-Situ* Digestion



# Land required in Brazil





# Supply US Gasoline Consumption

$$\text{Plants} = \frac{130 \times 10^9 \text{ gal gas}}{\text{yr}} \times \frac{1.2 \text{ gal alc}}{\text{gal gas}} \times \frac{\text{plant} \cdot \text{yr}}{629 \times 10^6 \text{ gal alc}} = 248 \text{ plants}$$

$$\text{Area} = 248 \text{ plants} \times \frac{366 \text{ mi}^2}{\text{plant}} = 90,900 \text{ mi}^2$$



302 mi



# Expected Product Yields (mesophilic 40°C)

$$\text{Total Acid} = 24 \frac{\text{tonne biomass}}{\text{h}} \times \frac{8000 \text{ h}}{\text{yr}} \times \frac{0.49 \text{ tonne acid}}{\text{tonne biomass}} \times \frac{2200 \text{ lb}}{\text{tonne}} = 207 \frac{\text{mill lb}}{\text{yr}}$$

## Plant Production

$$\text{C2} = 207 \frac{\text{mill lb total acid}}{\text{yr}} \times \frac{0.41 \text{ lb C2}}{\text{lb total acid}} = 85 \frac{\text{mill lb}}{\text{yr}}$$

$$\text{C3} = 207 \frac{\text{mill lb total acid}}{\text{yr}} \times \frac{0.15 \text{ lb C3}}{\text{lb total acid}} = 31 \frac{\text{mill lb}}{\text{yr}}$$

$$\text{C4}^+ = 207 \frac{\text{mill lb total acid}}{\text{yr}} \times \frac{0.44 \text{ lb C4}^+}{\text{lb total acid}} = 91 \frac{\text{mill lb}}{\text{yr}}$$

## US Production

$$3700 \frac{\text{mill lb}}{\text{yr}} \quad (2.3\%)$$

$$250 \frac{\text{mill lb}}{\text{yr}} \quad (12.4\%)$$



# Expected Product Yields (thermophilic 55°C)

$$\text{Total Acid} = 24 \frac{\text{tonne biomass}}{\text{h}} \times \frac{8000 \text{ h}}{\text{yr}} \times \frac{0.49 \text{ tonne acid}}{\text{tonne biomass}} \times \frac{2200 \text{ lb}}{\text{tonne}} = 207 \frac{\text{mill lb}}{\text{yr}}$$

## Plant Production

$$C2 = 207 \frac{\text{mill lb total acid}}{\text{yr}} \times \frac{0.80 \text{ lb C2}}{\text{lb total acid}} = 166 \frac{\text{mill lb}}{\text{yr}}$$

$$C3 = 207 \frac{\text{mill lb total acid}}{\text{yr}} \times \frac{0.04 \text{ lb C3}}{\text{lb total acid}} = 8.3 \frac{\text{mill lb}}{\text{yr}}$$

$$C4^+ = 207 \frac{\text{mill lb total acid}}{\text{yr}} \times \frac{0.16 \text{ lb C4}^+}{\text{lb total acid}} = 33 \frac{\text{mill lb}}{\text{yr}}$$

## US Production

$$3700 \frac{\text{mill lb}}{\text{yr}} \quad (4.5\%)$$

$$250 \frac{\text{mill lb}}{\text{yr}} \quad (3.3\%)$$



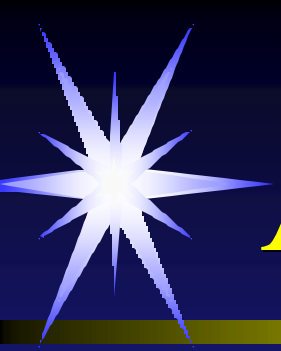
# Lime Treatment

$T = 100^{\circ}\text{C}$

$t = 1 \text{ h}$

Lime loading =  $0.1 \text{ g Ca(OH)}_2/\text{g biomass}$

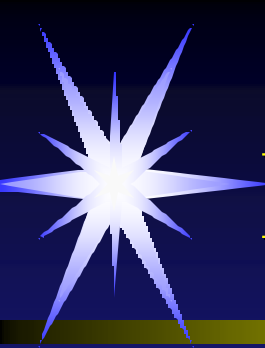
Water loading =  $5 \text{ to } 15 \text{ g H}_2\text{O}/\text{g biomass}$



# Affordable Fermentors

Above-ground stainless steel	\$380/m <sup>3</sup>
Above-ground carbon steel	\$125/m <sup>3</sup>
Above-ground concrete	\$ 69/m <sup>3</sup>
In-ground plastic	\$ 12/m <sup>3</sup>





# Heat Requirements

Btu  
lb water removed

Single-effect evaporator	1000
Triple-effect evaporator	333
Amine dewatering	60