MixAlco Process

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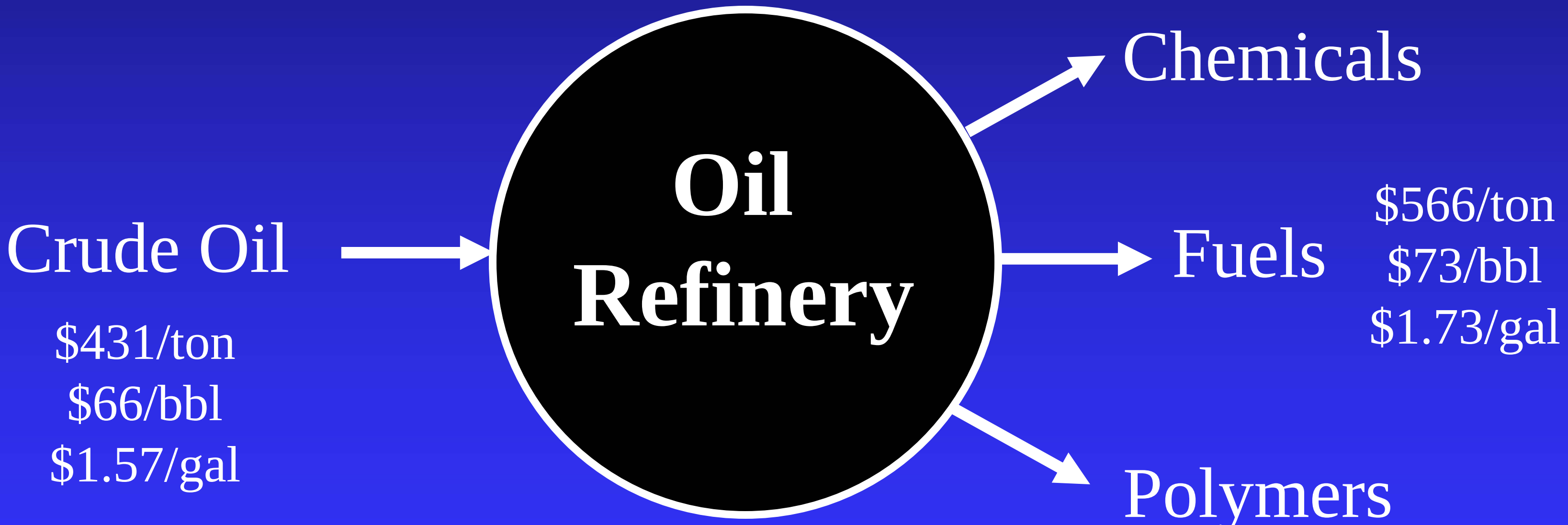
1876

Oil Refinery



Crude Oil

$431/ton
$66/bbl
$1.57/gal

Oil Refinery

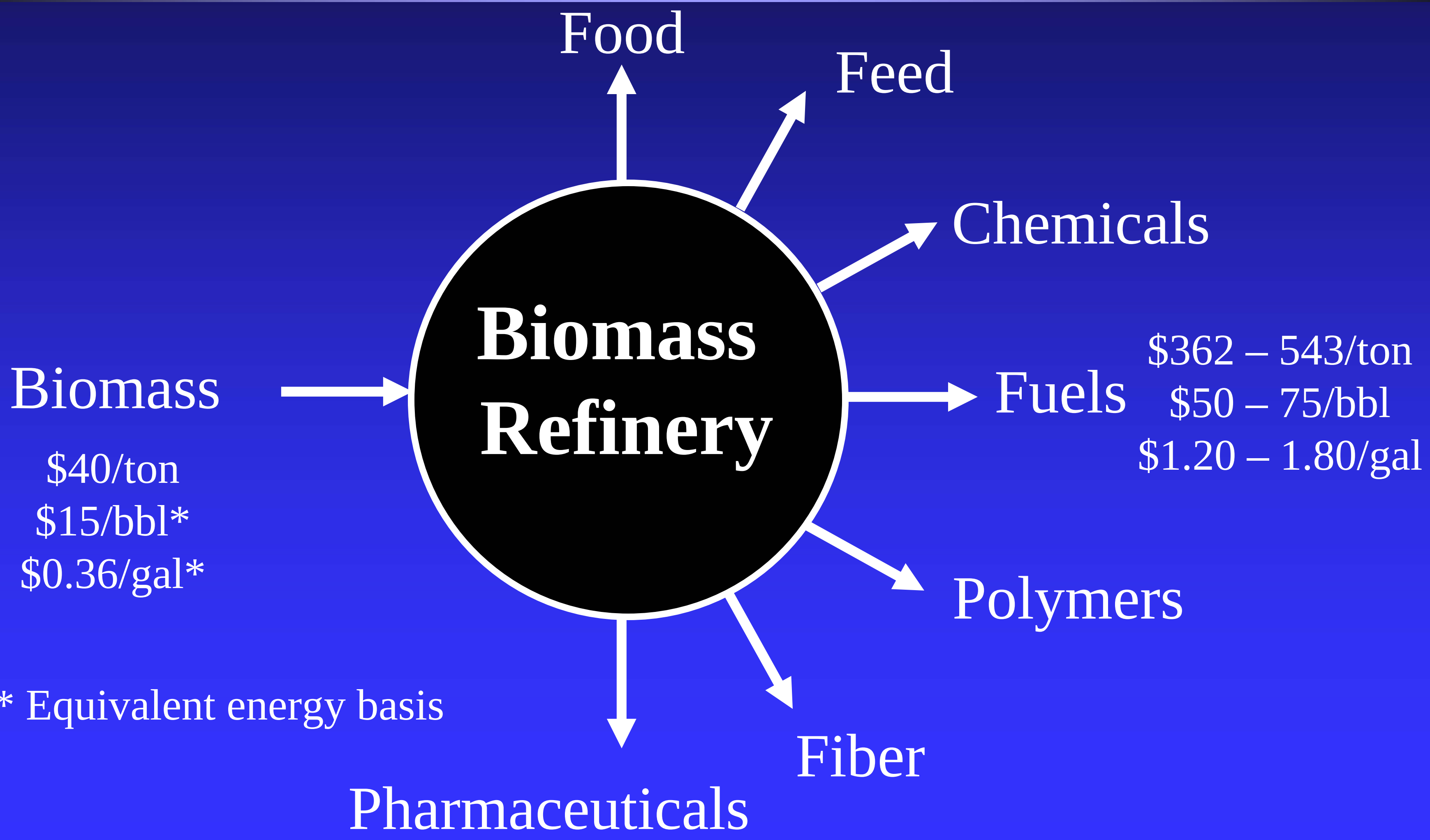
Chemicals

Fuels

$566/ton
$73/bbl
$1.73/gal

Polymers

Biomass Refinery



Biomass

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

Biomass Refinery

Food

Feed

Chemicals

Fuels

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

Polymers

Fiber

Pharmaceuticals

* Equivalent energy basis

Chemicals: Thermochemical platform

$$\text{Lignocellulose} \xrightarrow[\text{Gasify}]{} \begin{matrix} CO \\ H_2 \end{matrix} \xrightarrow[\text{Catalyst}]{} \text{Chemicals}$$

(Syngas)

Fischer Tropsch fuels
Methanol
Mixed alcohols
Ammonia

Chemicals: Thermochemical platform

$$\text{Lignocellulose} \xrightarrow[\text{Gasify}]{\qquad} \begin{matrix} CO \\ H_2 \end{matrix} \xrightarrow[\text{Catalyst}]{\qquad} \text{Chemicals}$$

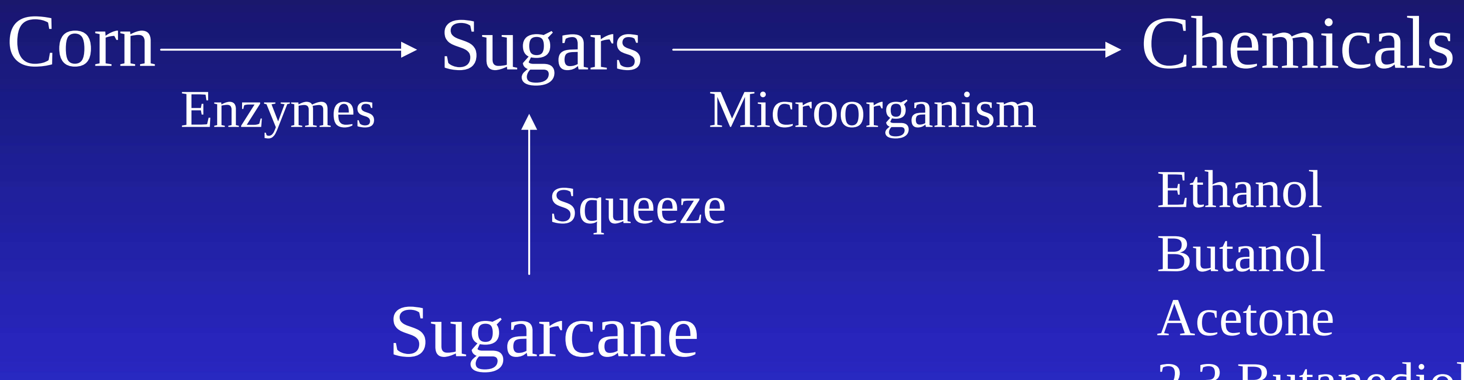
(Syngas)

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

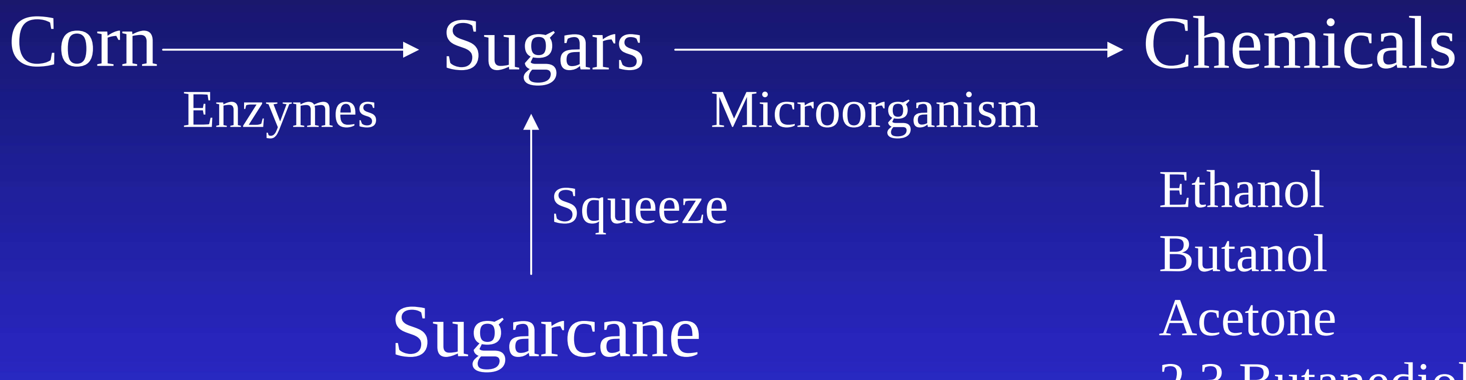
Microorganism

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



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

Disadvantages

- Limited availability
- Competition with food
- Requires sterility
- Difficult separations

Chemicals: Sugar platform (2nd Generation)

Lignocellulose $\xrightarrow[\text{Enzymes}]{}$ Sugars $\xrightarrow[\text{Microorganism}]{}$ Chemicals

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

Chemicals: Sugar platform (2^{nd} Generation)

$$\text{Lignocellulose} \xrightarrow[\text{Enzymes}]{} \text{Sugars} \xrightarrow[\text{Microorganism}]{} \text{Chemicals}$$

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

Disadvantages

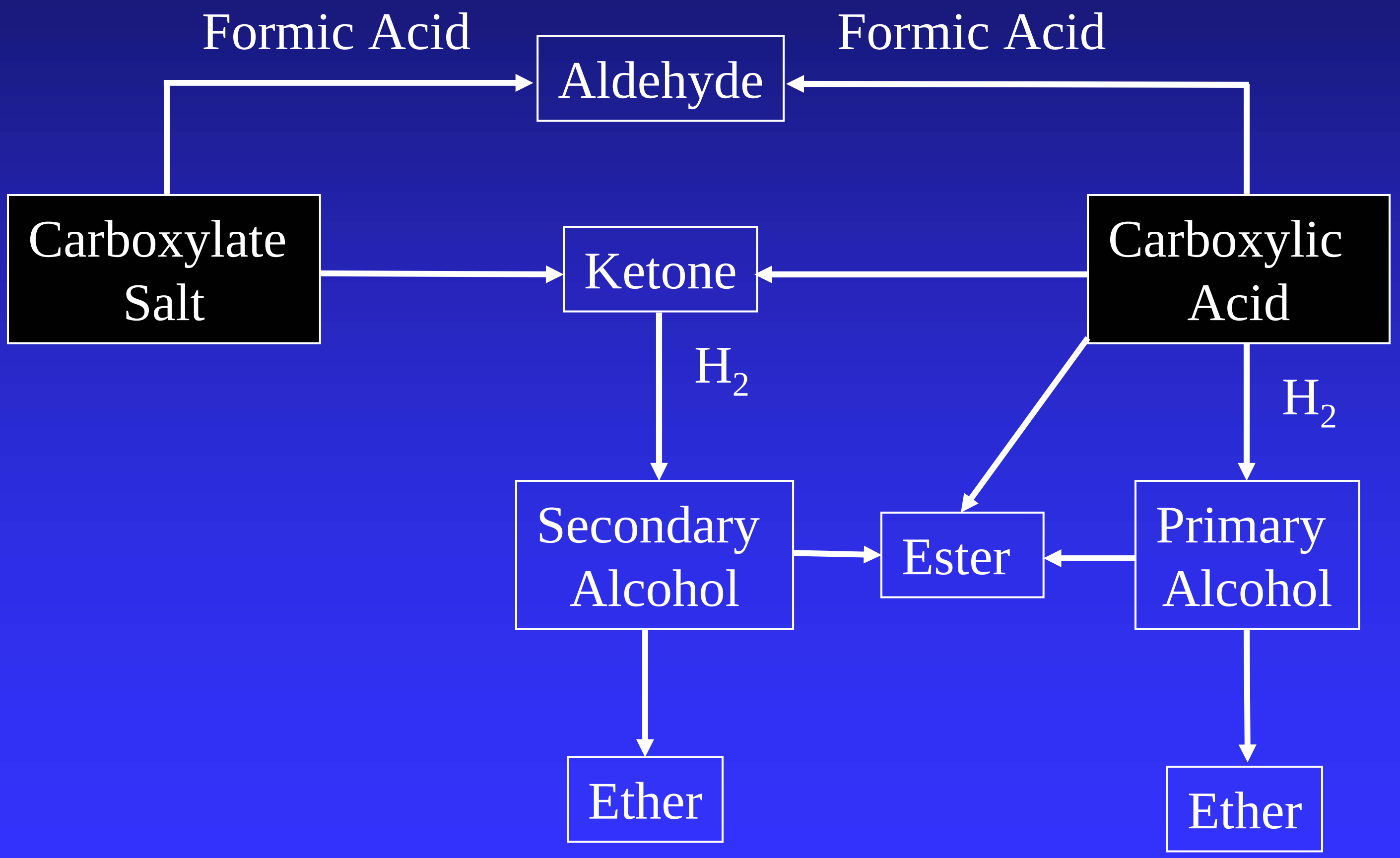
- Requires sterility
- Expensive enzymes
- Difficult to use all sugars
- Uses GMOs
- Lignin not converted to liquid fuels
- Extensive pretreatment required
- Difficult to supply enough biomass to achieve economy of scale

Chemicals: Mixed Acids platform

Lignocellulose $\xrightarrow[\text{Mixed-Culture Microorganisms}]{}$ Carboxylic acids/salts $\xrightarrow[\text{Chemistry}]{}$ Chemicals

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

Chemical Flowchart


Formic Acid
Aldehyde
Formic Acid
Carboxylate Salt
Ketone
Carboxylic Acid
H_2
H_2
Secondary Alcohol
Ester
Primary Alcohol
Ether
Ether

Anaerobic Digestion

Biomass (cellulose, starch, proteins, fats)

↓ Mixed culture of microorganisms

Hydrolysis → Acidogenesis → Acetogenesis

Hydrolysis: (free sugars, amino acids, fatty acids)

Acidogenesis: (Carboxylic acids, NH_3, CO_2, H_2S)

Acetogenesis: (Acetic Acid, CO_2, H_2)

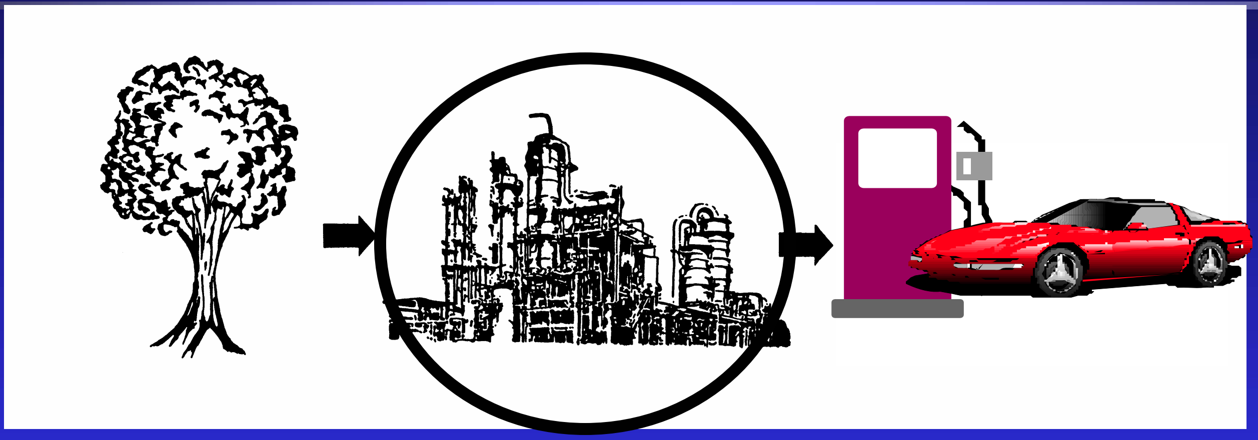
↓

~~Methanogenesis~~

~~(CH_4, CO_2)~~

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

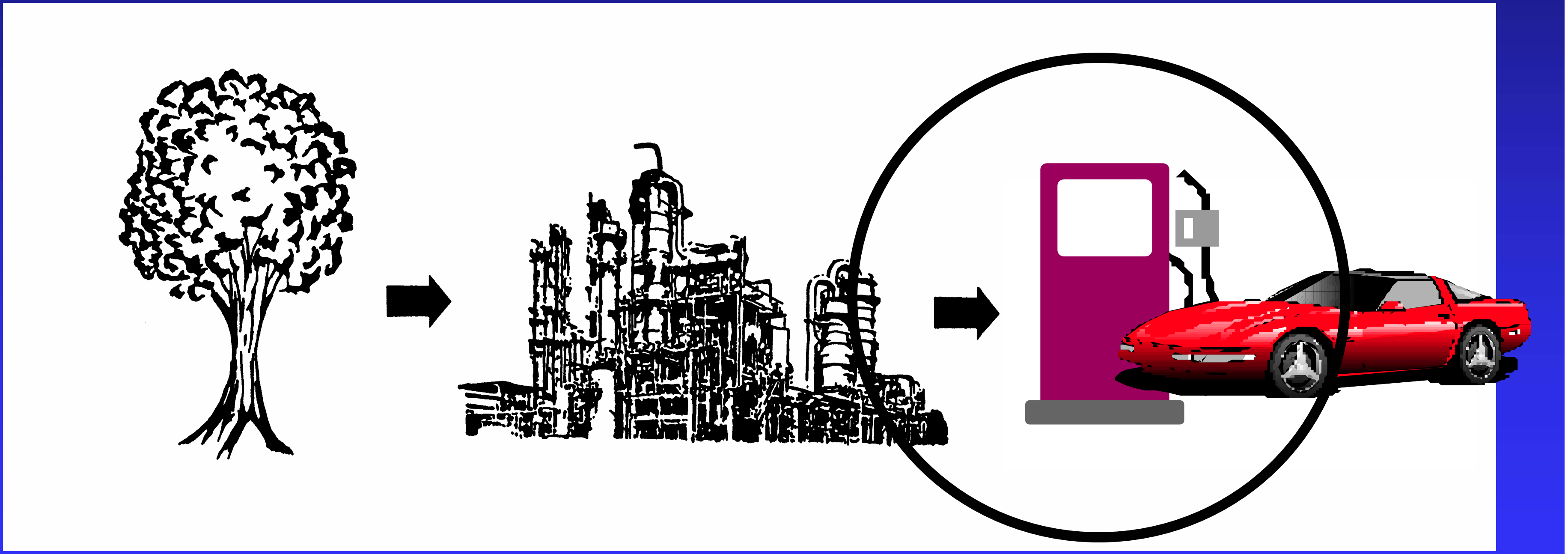
Desirable Process Properties



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

	Ethanol	MTBE	Mixed Alcohols
Octane	high	high	high
Volatility	high	low	low
Pipeline shipping	no	yes	yes
Energy content	low	high	high
Heat of vaporization	high	low	low
Ground water damage	no	yes	no

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	*tert*-Butanol (TBA)	100
34	Isobutanol (IBA)	102
	Ethers	
55	Methy tertiary butyl ether (MTBE)	110
34	Di-isopropyl ether (DIPE)	105
17	Isopropyl tertiary butyl ether (IPTBE)	113

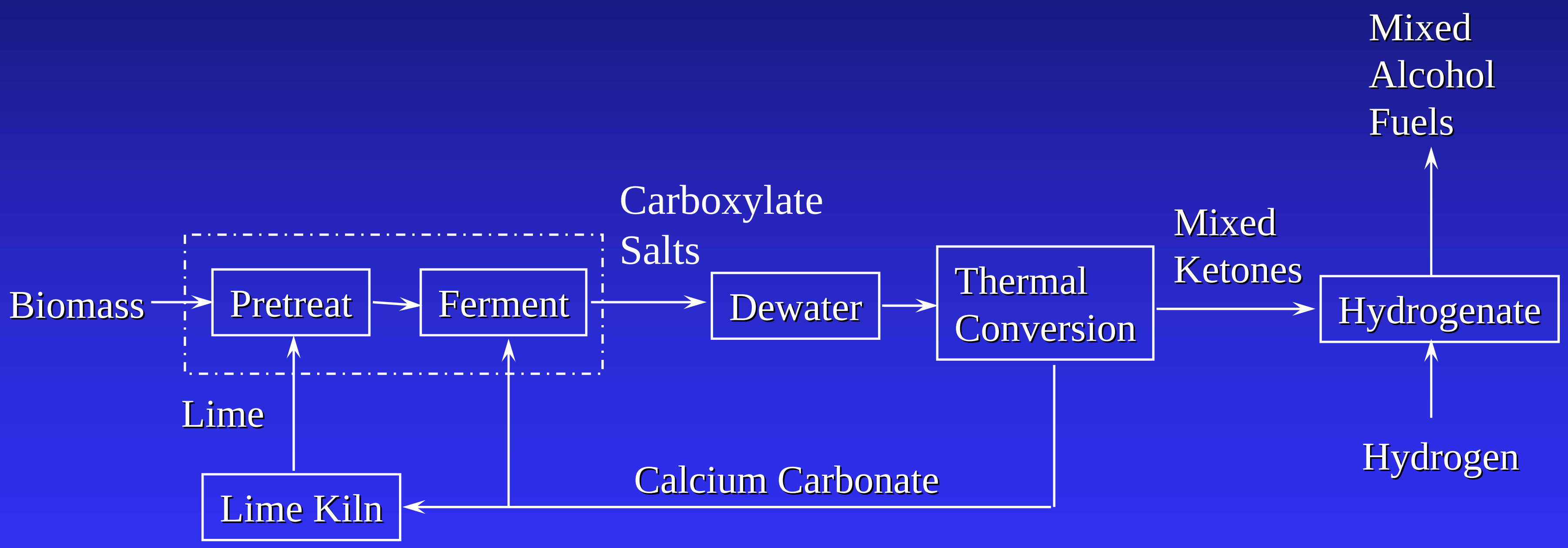
Klass, Biomass for Renewable Energy, Fuels, and Chemicals, Academic Press (1998).

Energy Content

	Energy	
	(MJ/L)	(Btu/gal)
Gasoline	34.9	125,000
Mixed Alcohols Version 1	29.0	104,000
Mixed Alcohols Version 2	26.5	95,000
Ethanol	23.4	84,300

MixAlco Process

MixAlco Process – Version 1


Mixed
Alcohol
Fuels

Carboxylate
Salts

Mixed
Ketones

Biomass

Pretreat

Ferment

Dewater

Thermal
Conversion

Hydrogenate

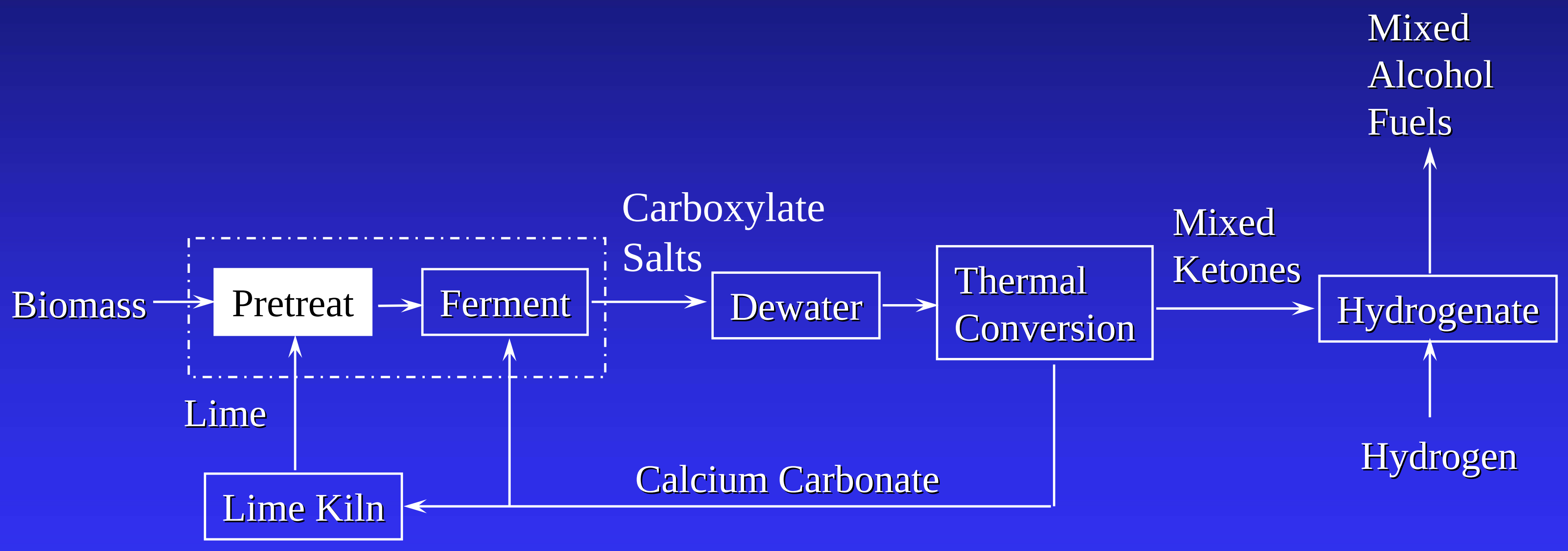
Lime

Hydrogen

Calcium Carbonate

Lime Kiln

Pretreatment



Biomass

Pretreat

Ferment

Carboxylate Salts

Dewater

Thermal Conversion

Mixed Ketones

Hydrogenate

Mixed Alcohol Fuels

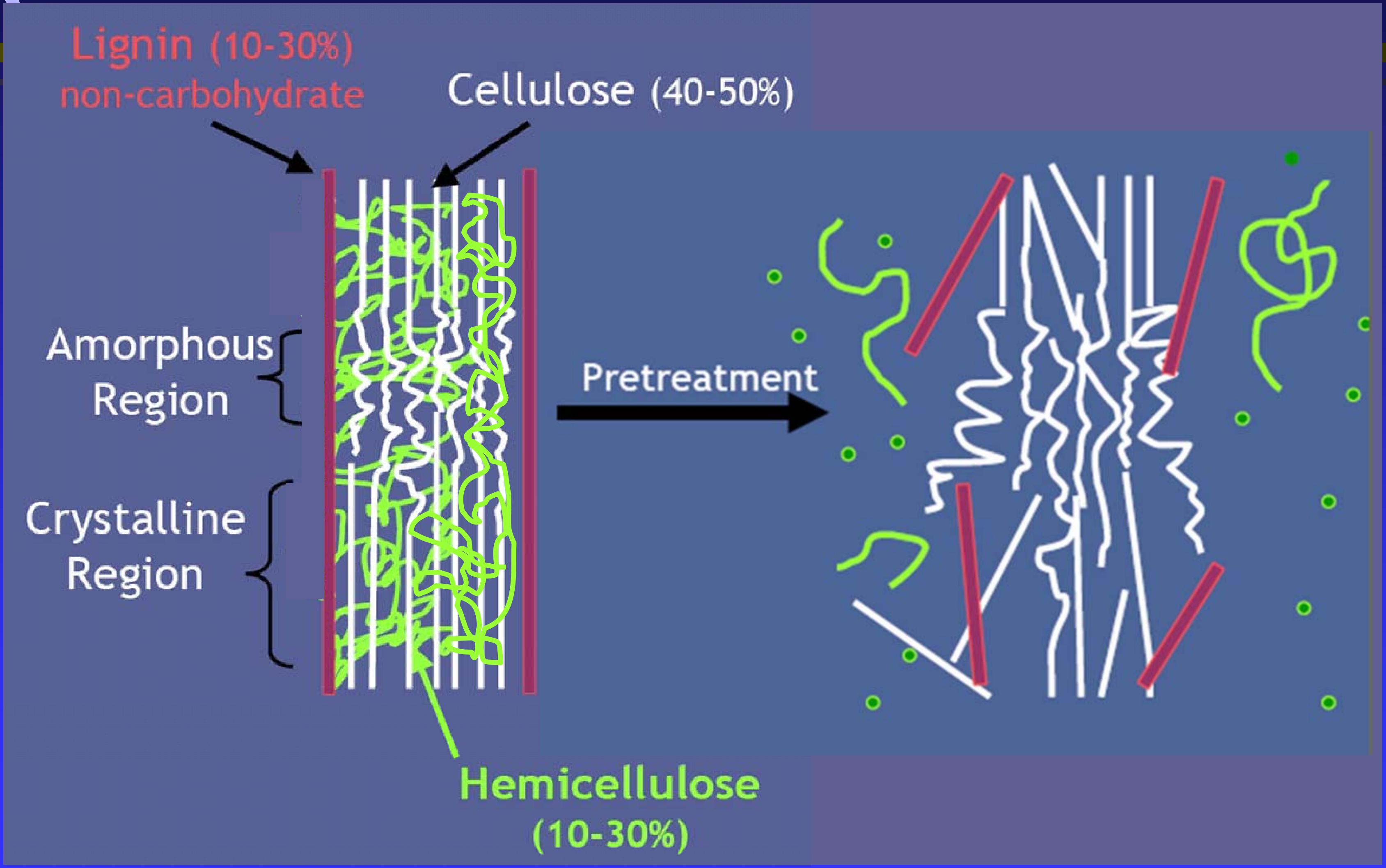
Hydrogen

Lime

Lime Kiln

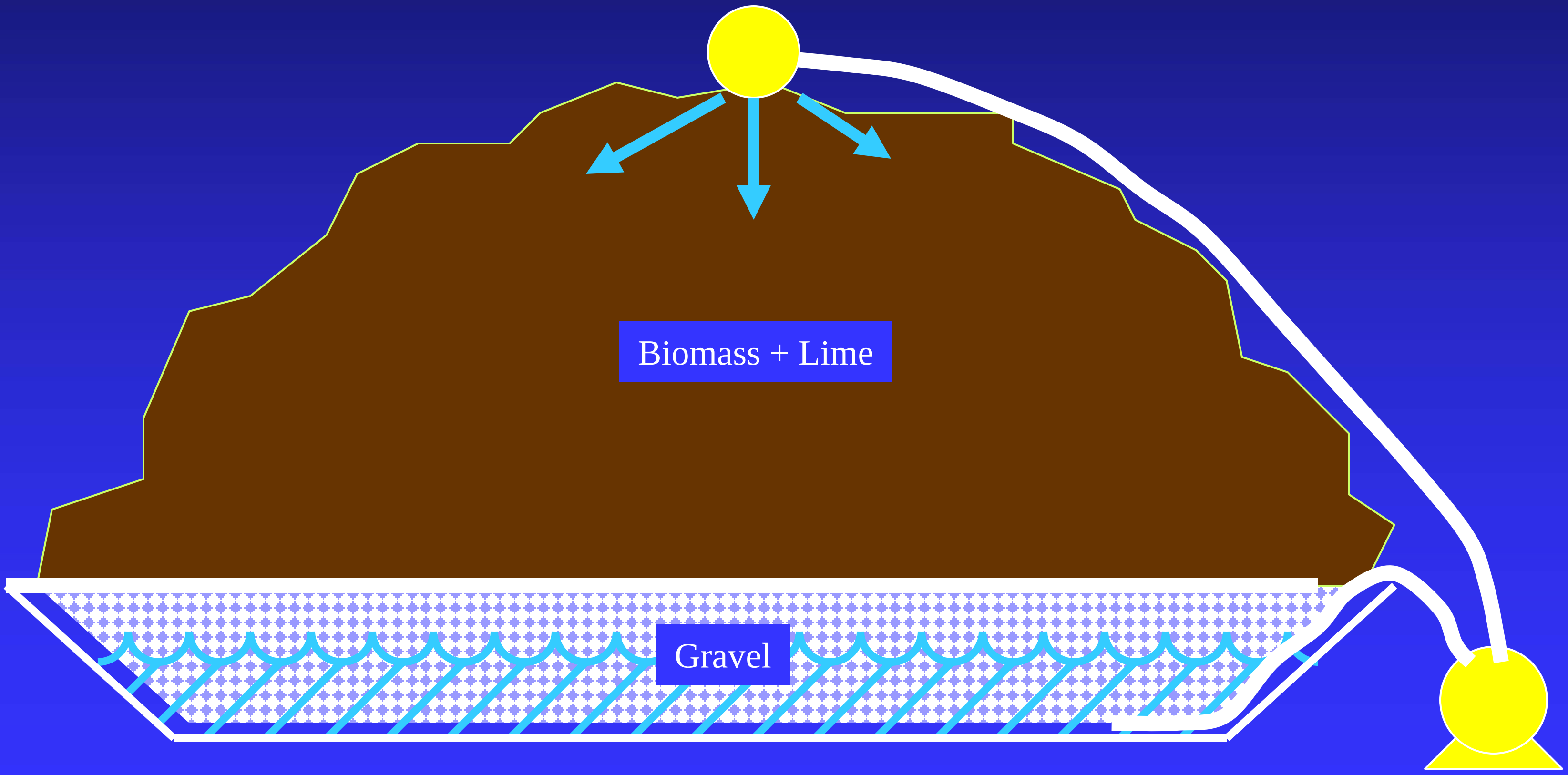
Calcium Carbonate

Pretreatment is needed

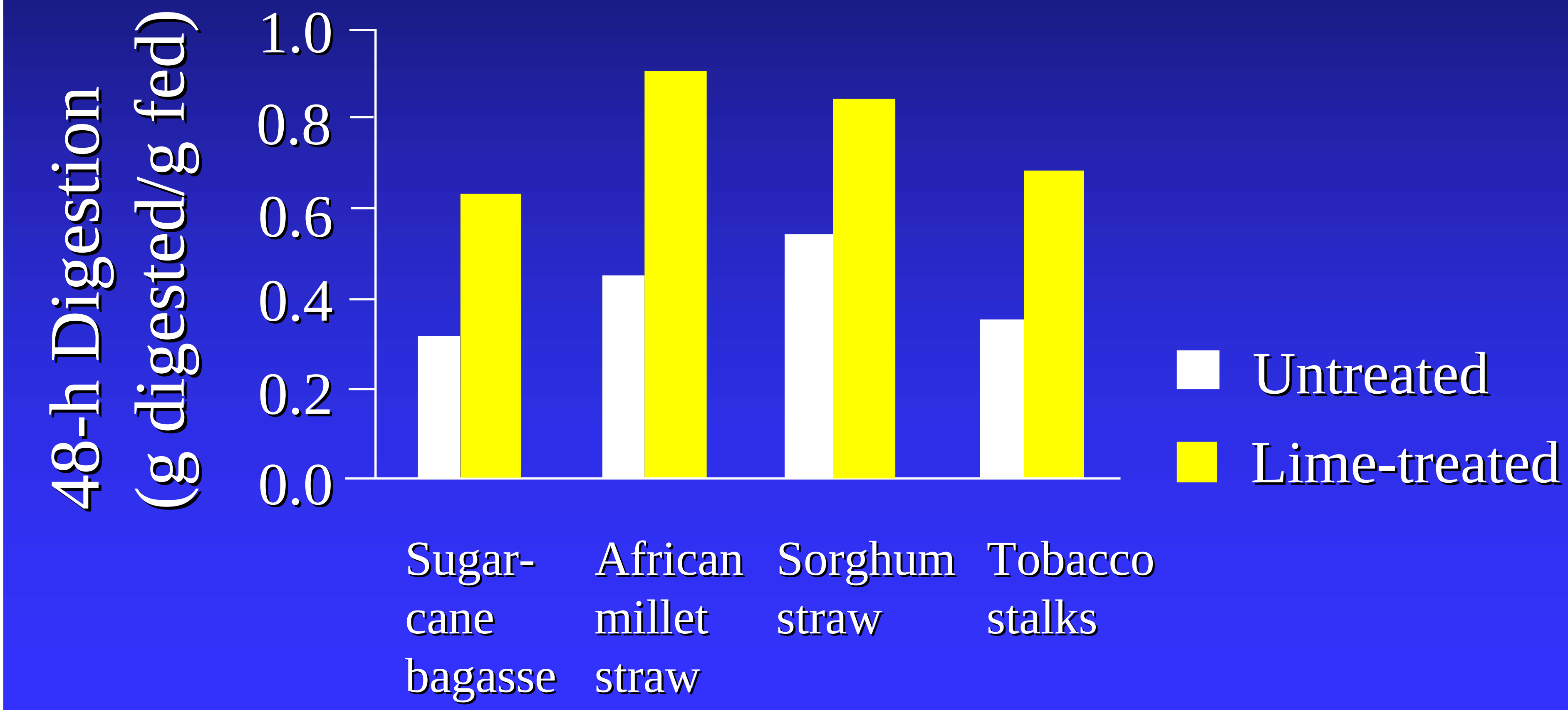


Source: Michael Ladisch, Purdue Univ.

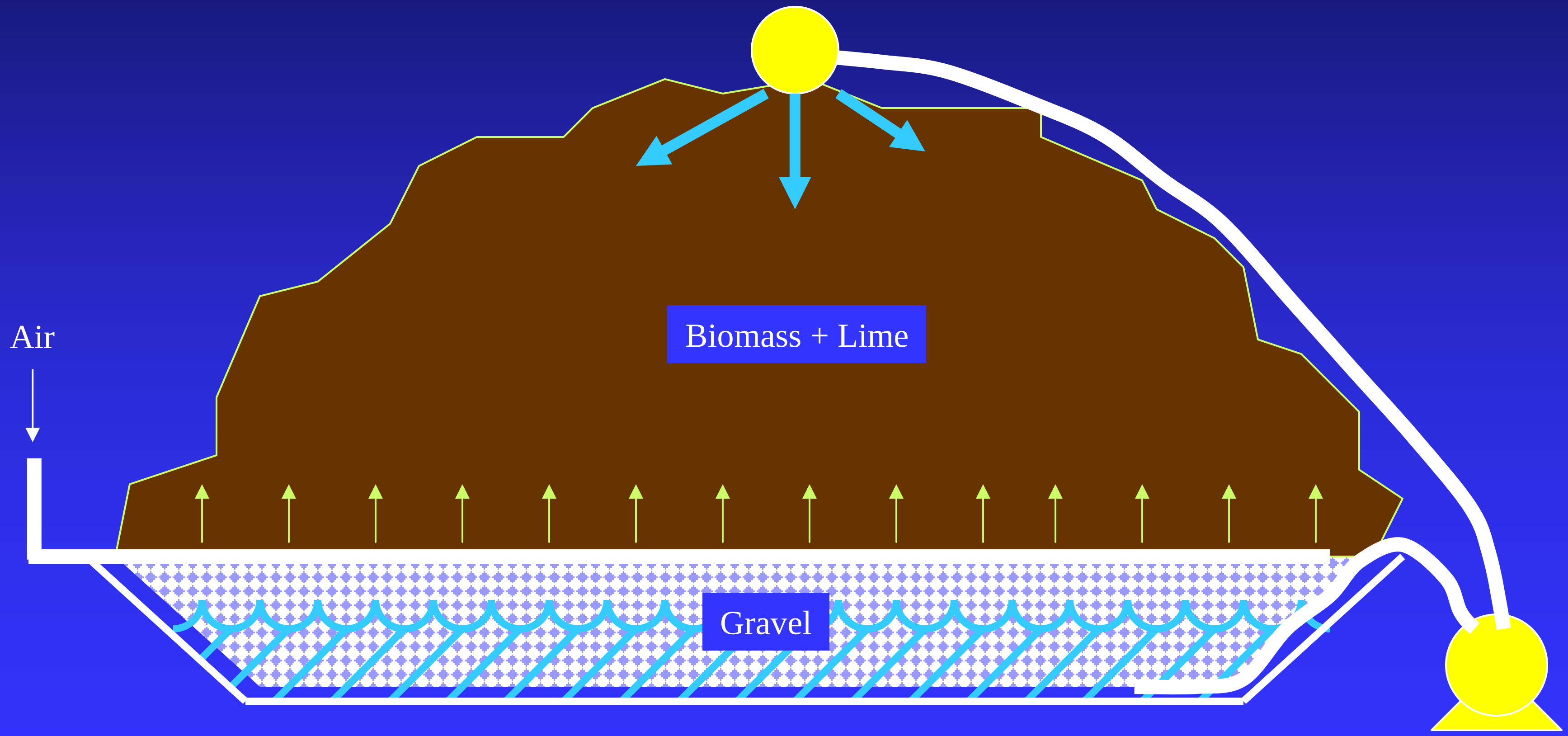
Lime Treatment



In-Situ Digestion

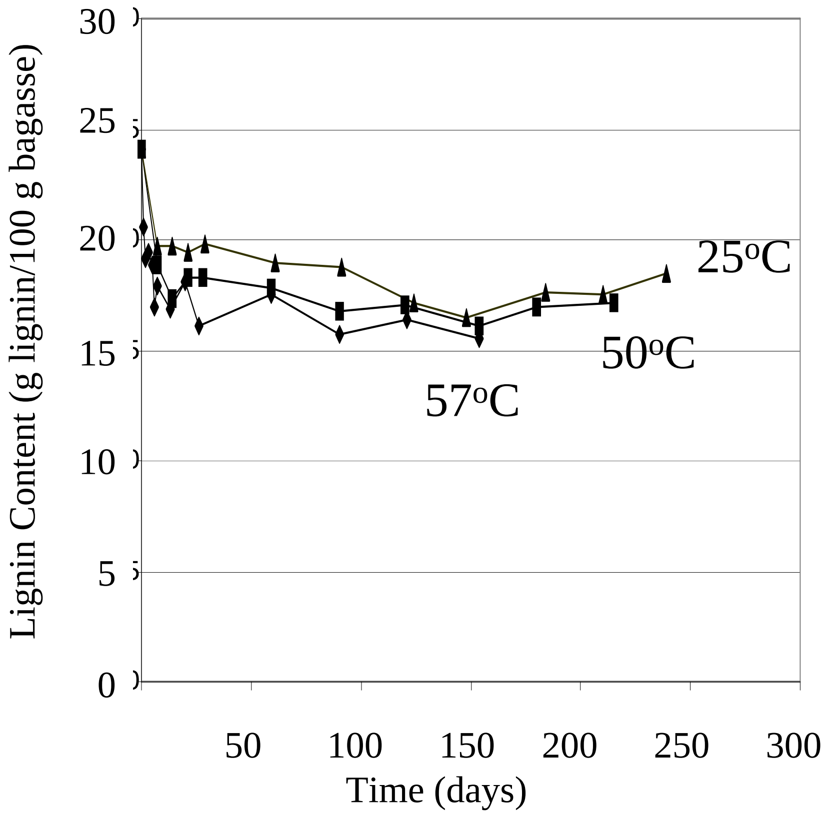


Advanced Lime Treatment

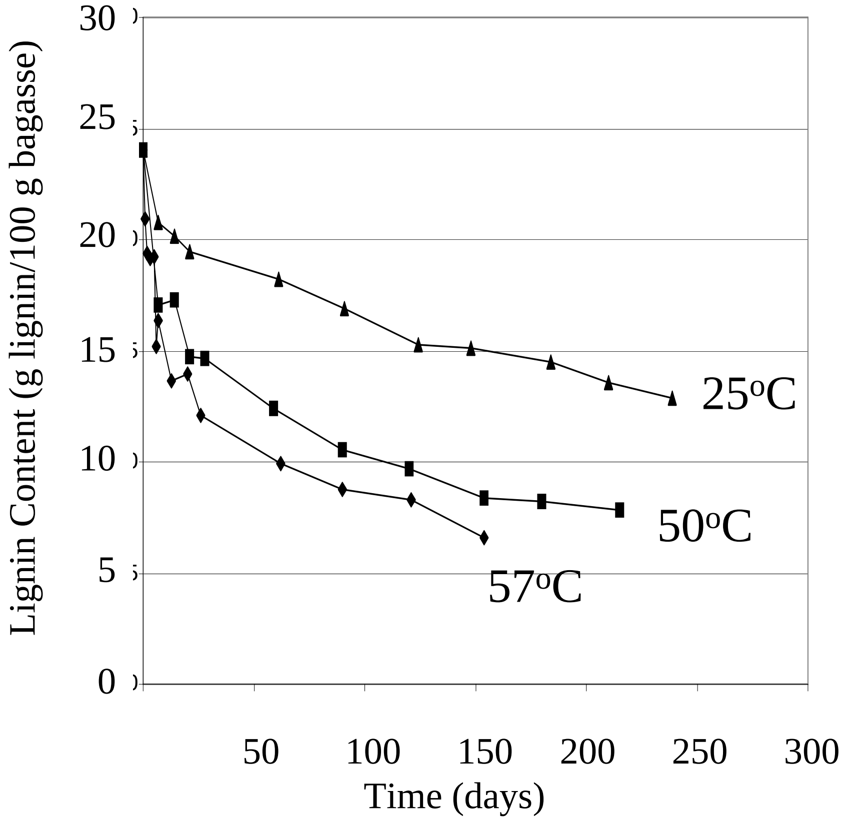


Lignin Removal

No Air

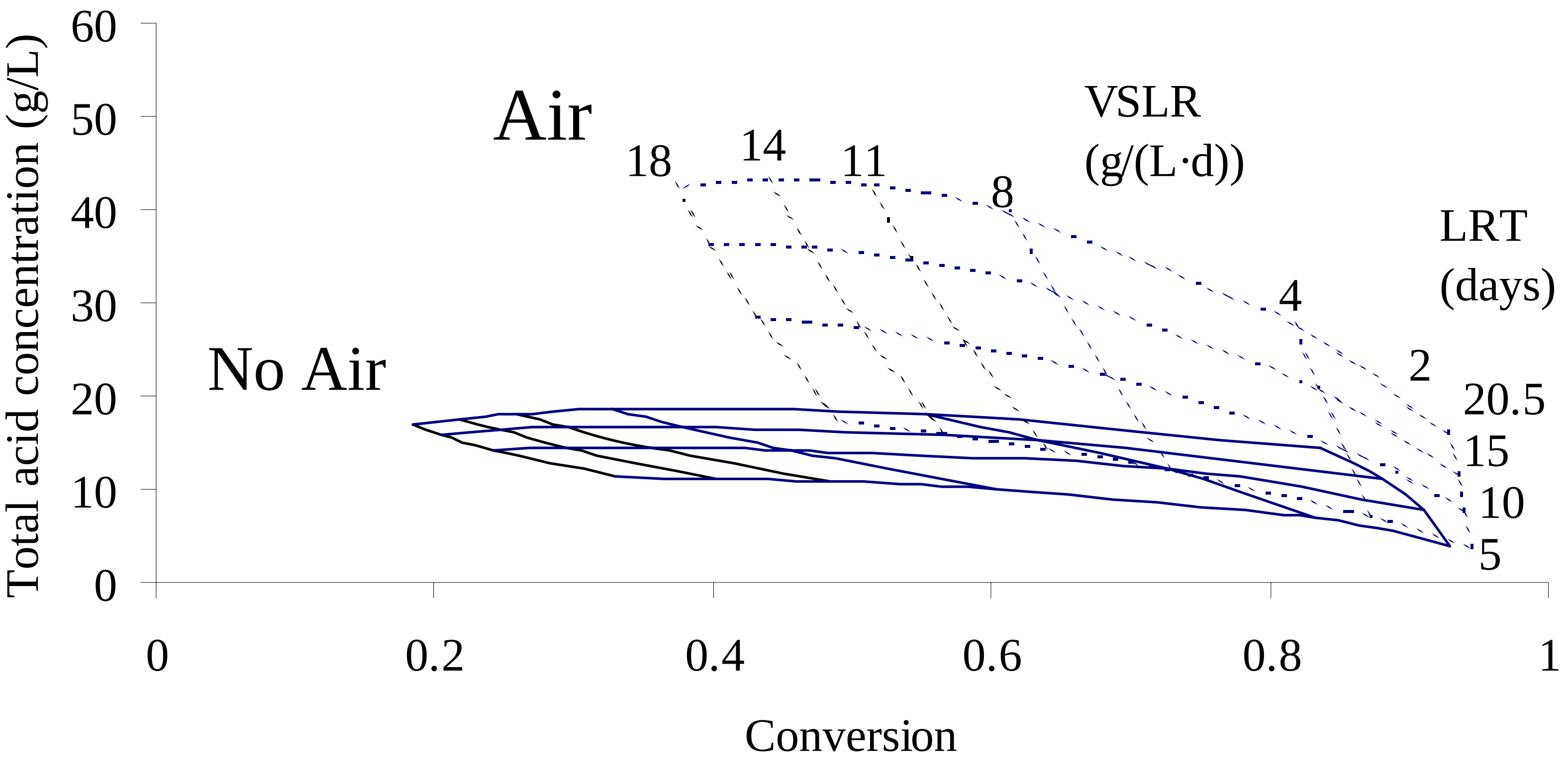


Air



Mixed-Acid Fermentation

Lime Treatment: 2 weeks, 25^{o}C
Terrestrial Inoculum



Building the Pile

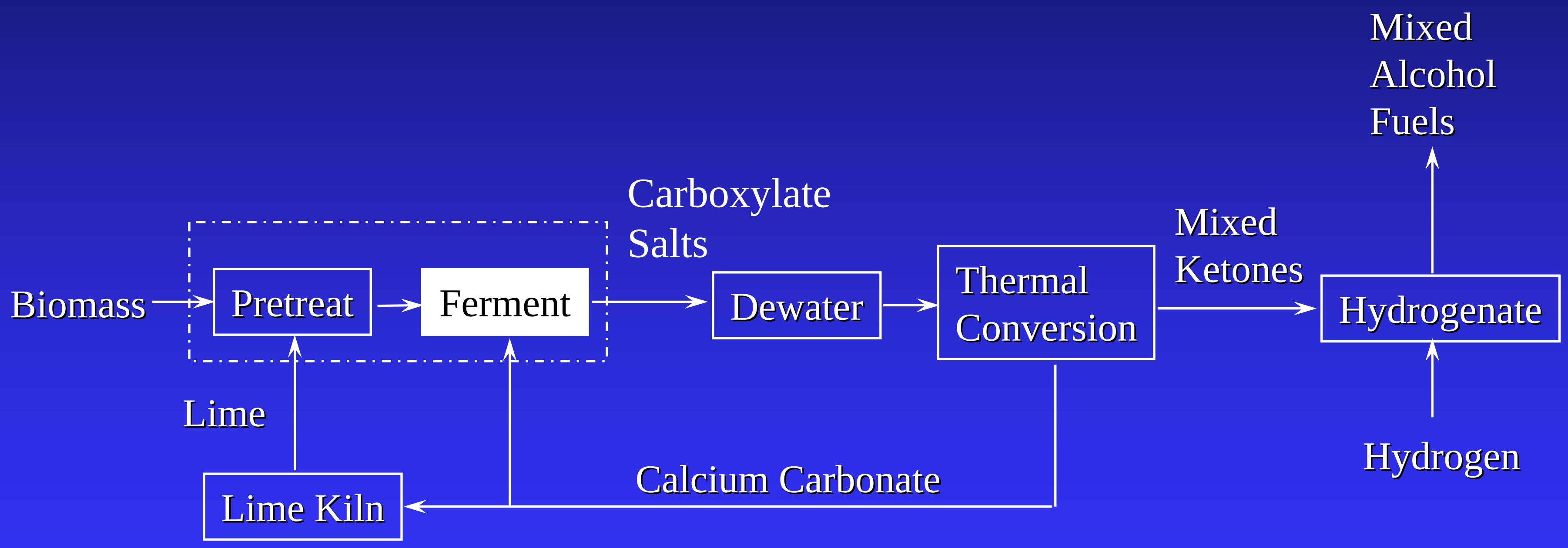
~100 ft

Building the Pile

Building the Pile

Crew directing the flow

Fermentation



Mixed
Alcohol
Fuels

Carboxylate
Salts

Mixed
Ketones

Biomass

Pretreat

Ferment

Dewater

Thermal
Conversion

Hydrogenate

Lime

Lime Kiln

Calcium Carbonate

Hydrogen

Environments where organic acids naturally form

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

Why are organic acids favored?

$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$ $\Delta G = -48.56$ kcal/mol

glucose ethanol

$C_6H_{12}O_6 \rightarrow 3\ C_2H_3OOH$ $\Delta G = -61.8$ kcal/mol

glucose acetic acid

The actual stoichiometry is more complex

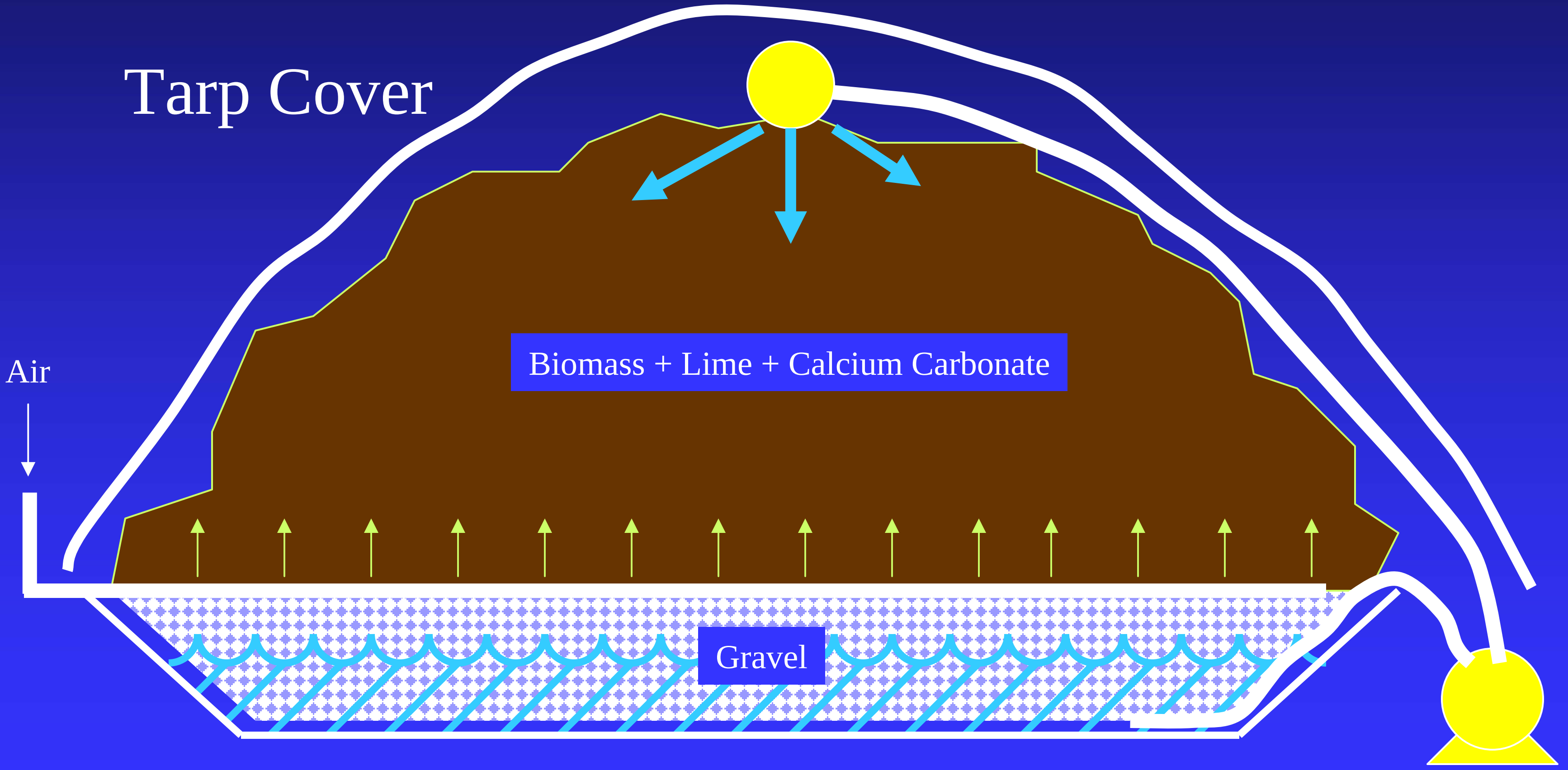
$C_6H_{12}O_6 \rightarrow$ acetate + propionate + butyrate + CO_2 + CH_4 + H_2O

Typical Product Spectrum at Different Culture 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	3 wt %	<1 wt %
	100 wt %	100 wt %


TANK
TANK
TANK
TANK

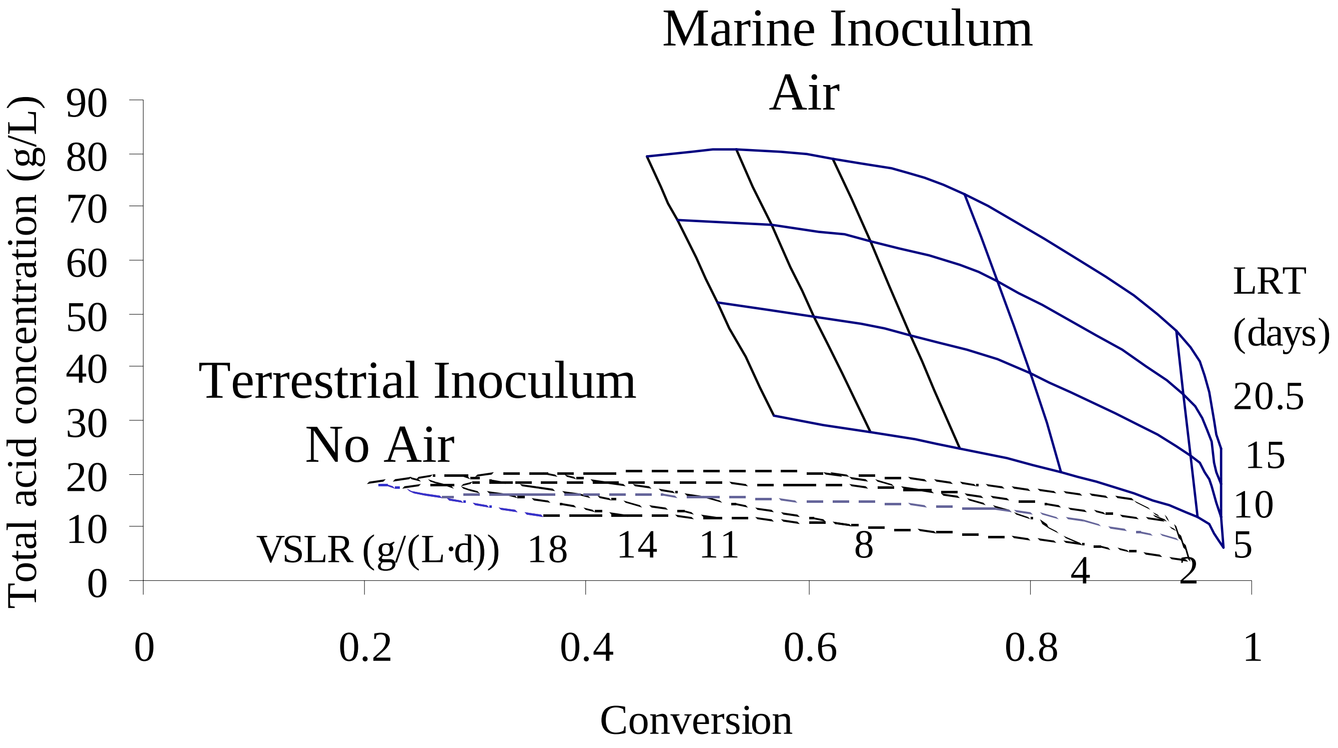
Storage + Pretreatment + Fermentation



Technology Evolution

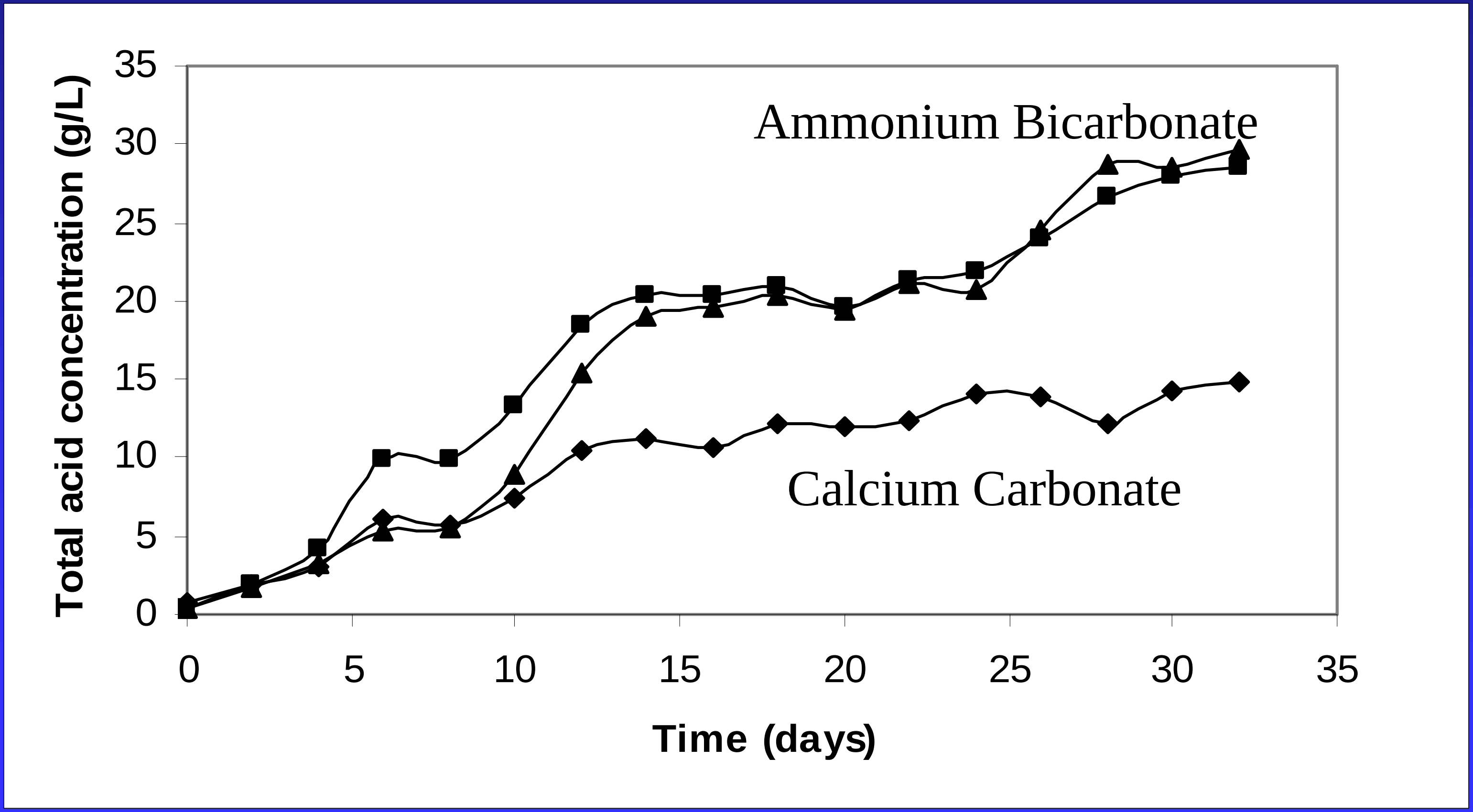
- Source of inoculum
- Type of buffer

Marine Inoculum



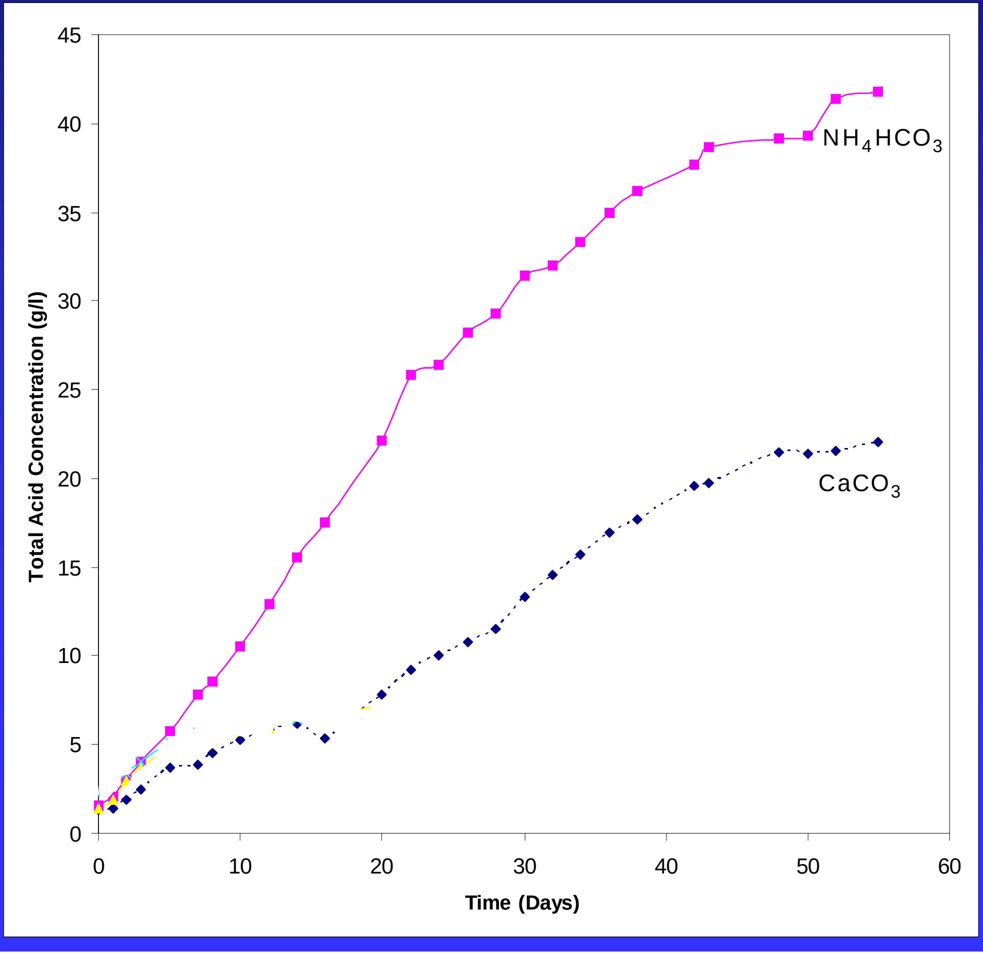
Ammonium Bicarbonate Buffer

40^{o}C

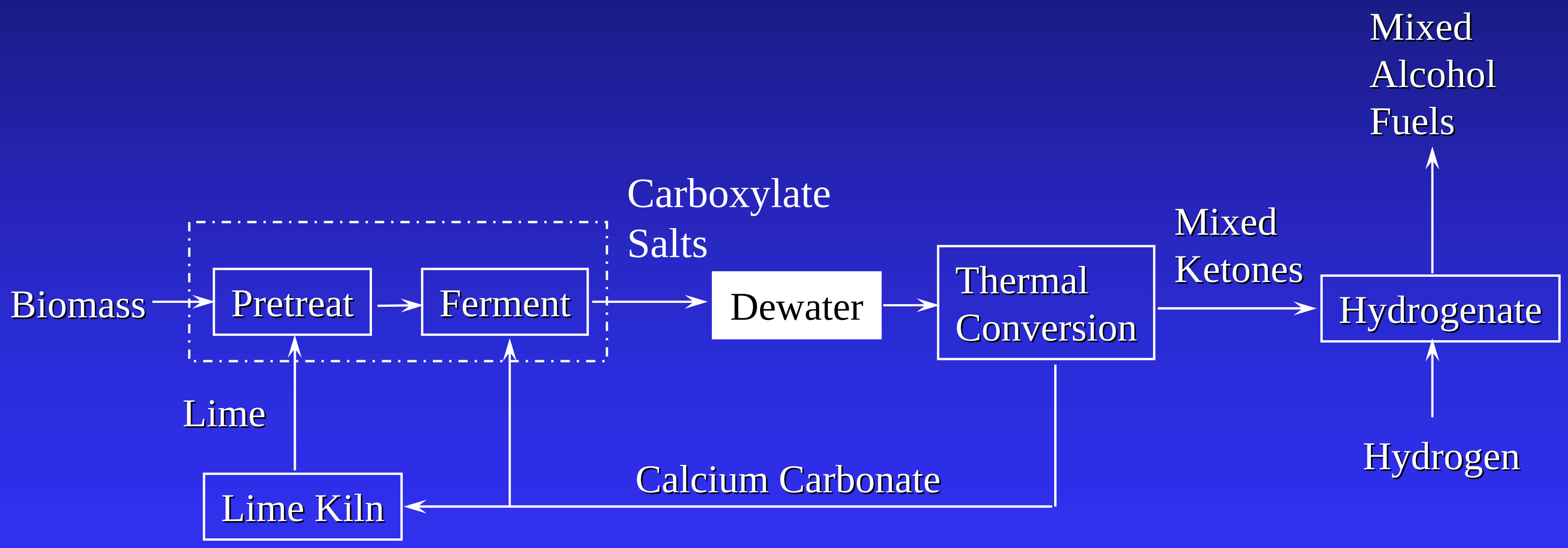


Ammonium Bicarbonate Buffer

55ºC



Dewatering



Mixed
Alcohol
Fuels

Carboxylate
Salts

Mixed
Ketones

Biomass

Pretreat

Ferment

Dewater

Thermal
Conversion

Hydrogenate

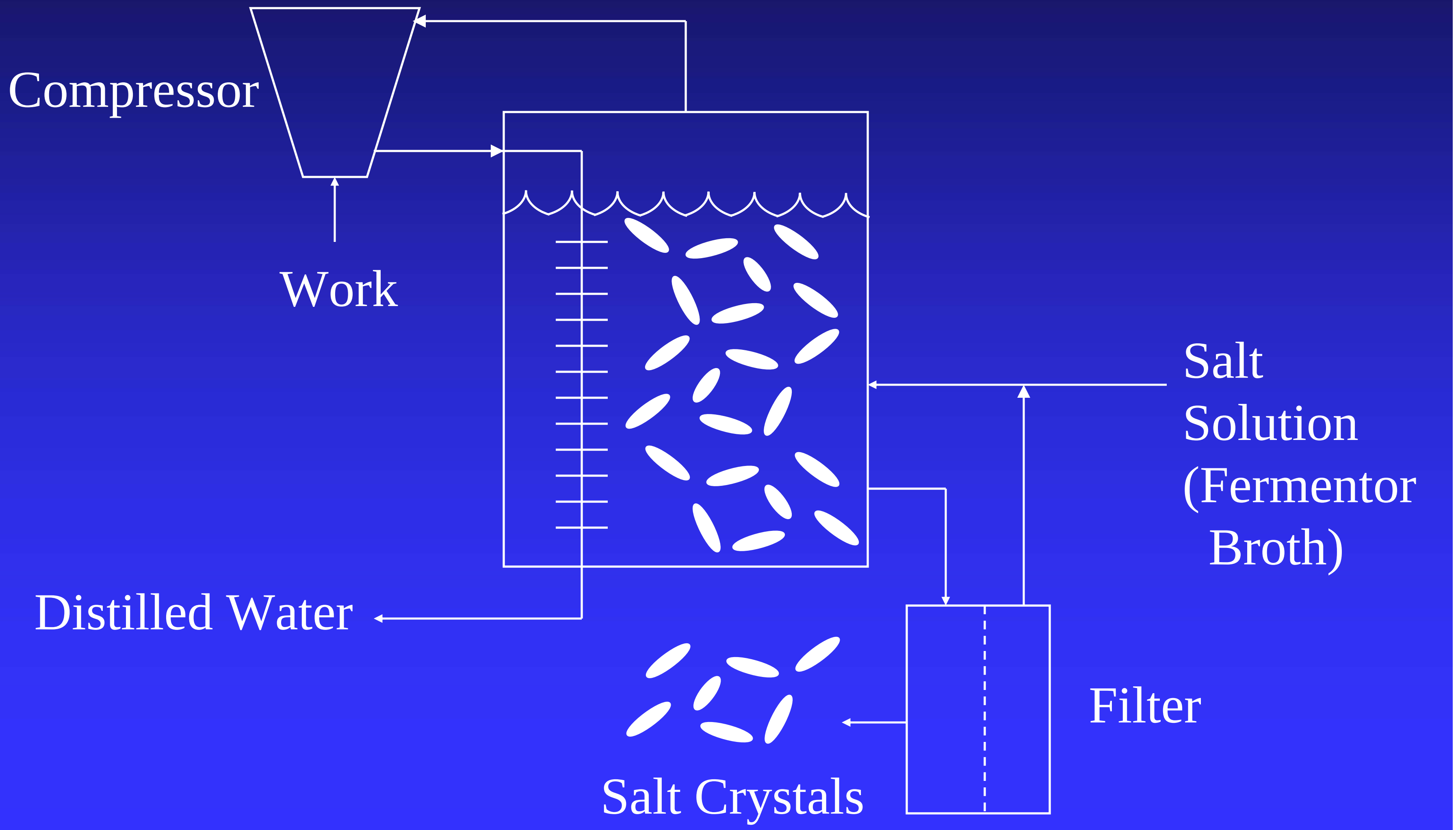
Lime

Lime Kiln

Calcium Carbonate

Hydrogen

Vapor-Compression Dewatering



Compressor

Work

Salt
Solution
(Fermentor
Broth)

Distilled Water

Filter

Salt Crystals

Dewatering Energetics

Ethanol Distillation (5% to 99.9%)

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

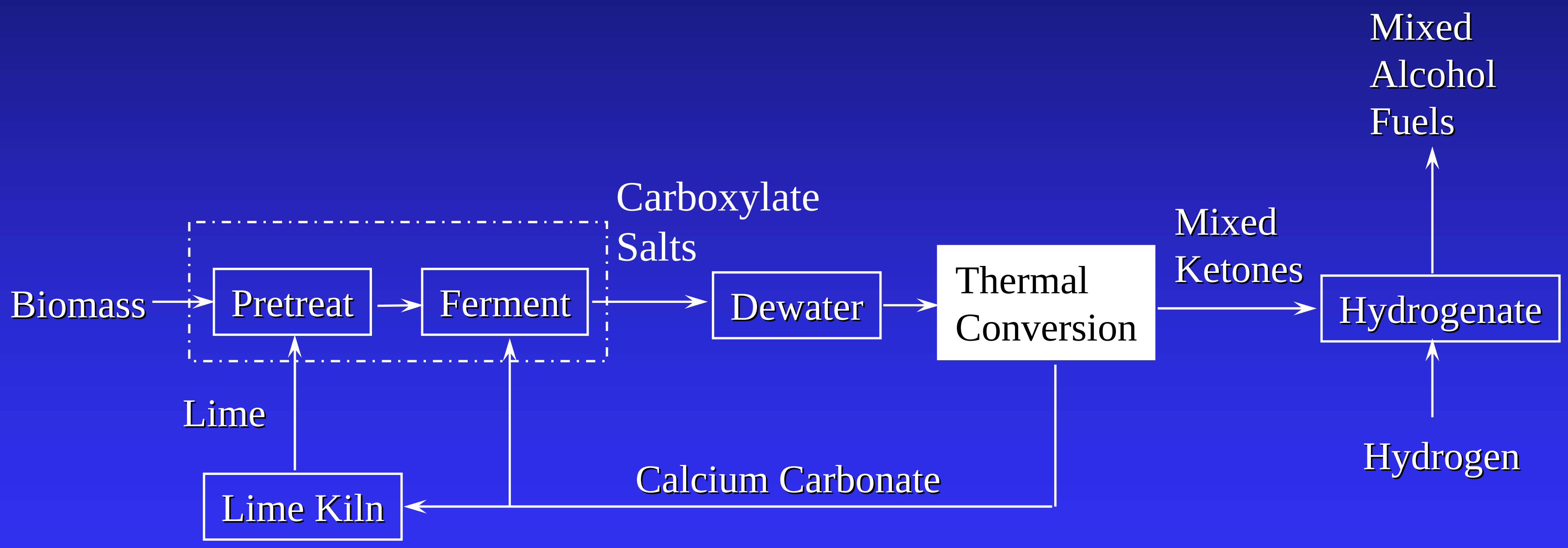
Source: B.L. Maiorella, Ethanol, *Comprehensive Biotechnology*, Vol. 3, Pergamon Press (1985).

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

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

Source: Jorge Lara, An Advanced Vapor-Compression Desalination System, PhD Dissertation, Texas A&M (2005).

Thermal Conversion



Biomass

Pretreat

Ferment

Carboxylate Salts

Dewater

Thermal Conversion

Mixed Ketones

Hydrogenate

Mixed Alcohol Fuels

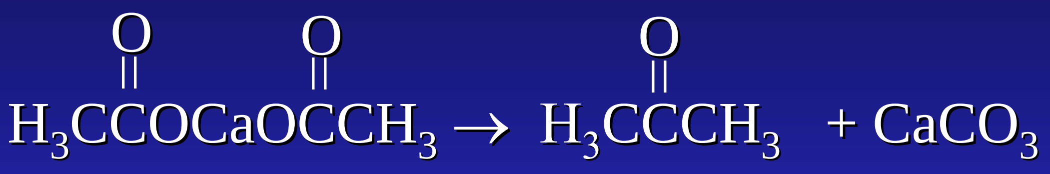
Hydrogen

Lime

Lime Kiln

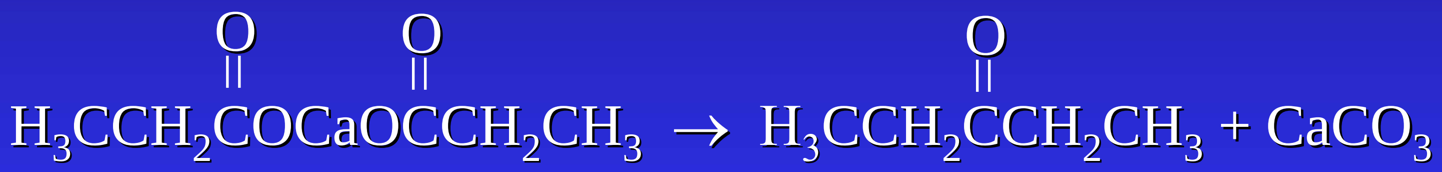
Calcium Carbonate

Thermal Conversion Stoichiometry



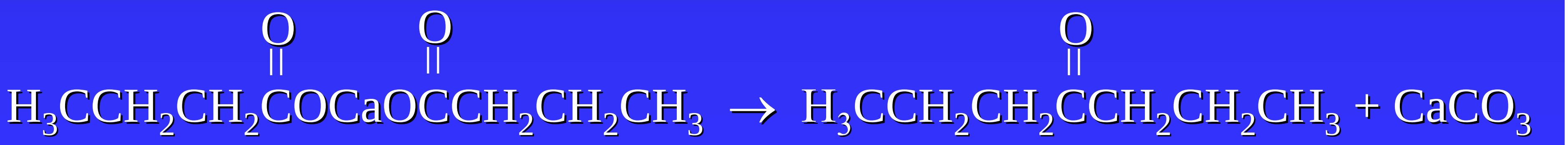
$$H_3C\overset{\overset{O}{\|}}{C}OCaO\overset{\overset{O}{\|}}{C}CH_3 \rightarrow H_3C\overset{\overset{O}{\|}}{C}CH_3 + CaCO_3$$

Calcium Acetate Acetone



$$H_3CCH_2\overset{\overset{O}{\|}}{C}OCaO\overset{\overset{O}{\|}}{C}CH_2CH_3 \rightarrow H_3CCH_2\overset{\overset{O}{\|}}{C}CH_2CH_3 + CaCO_3$$

Calcium Propionate Diethyl Ketone



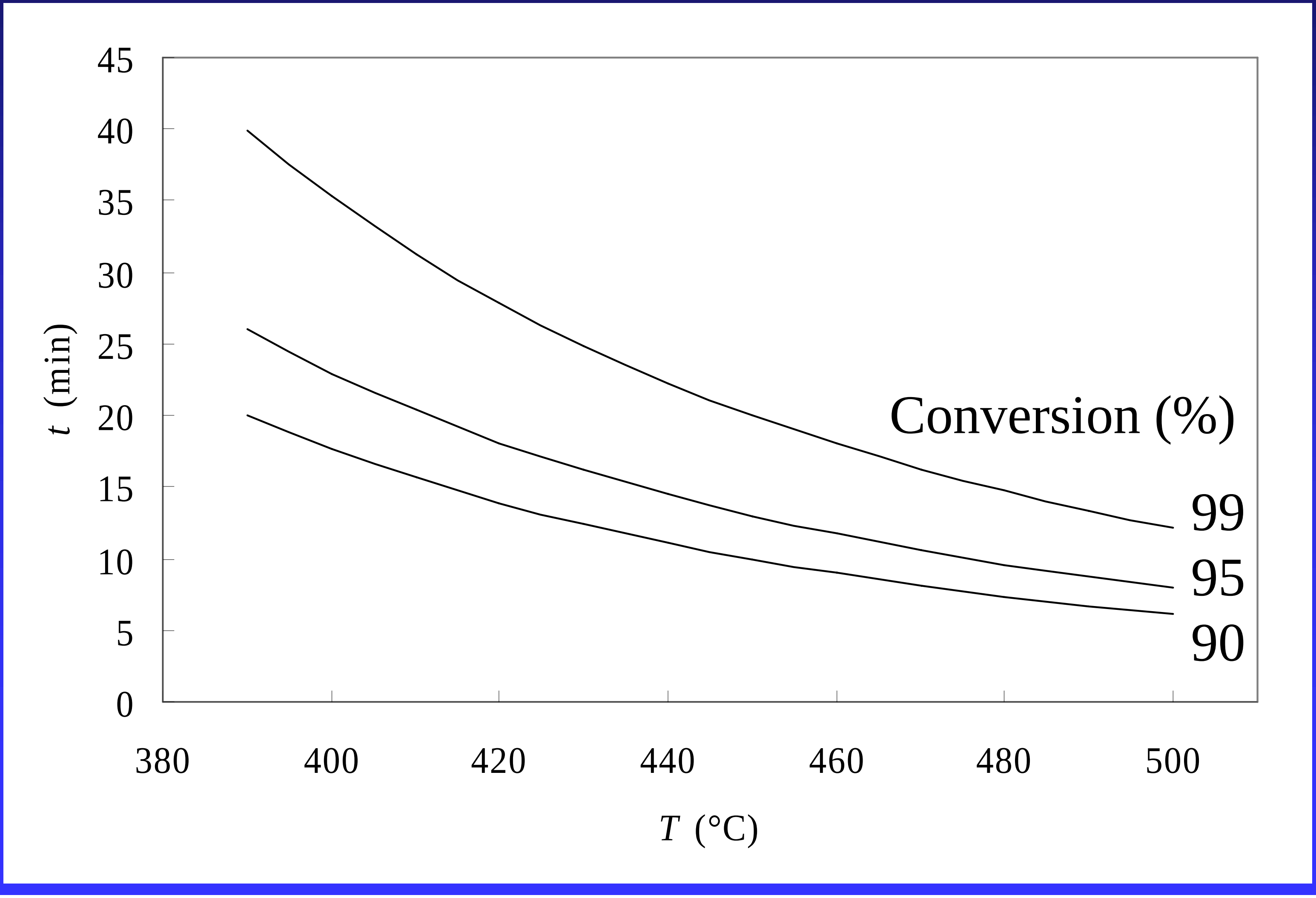
$$H_3CCH_2CH_2\overset{\overset{O}{\|}}{C}OCaO\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3 \rightarrow H_3CCH_2CH_2\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3 + CaCO_3$$

Calcium Butyrate Dipropyl Ketone

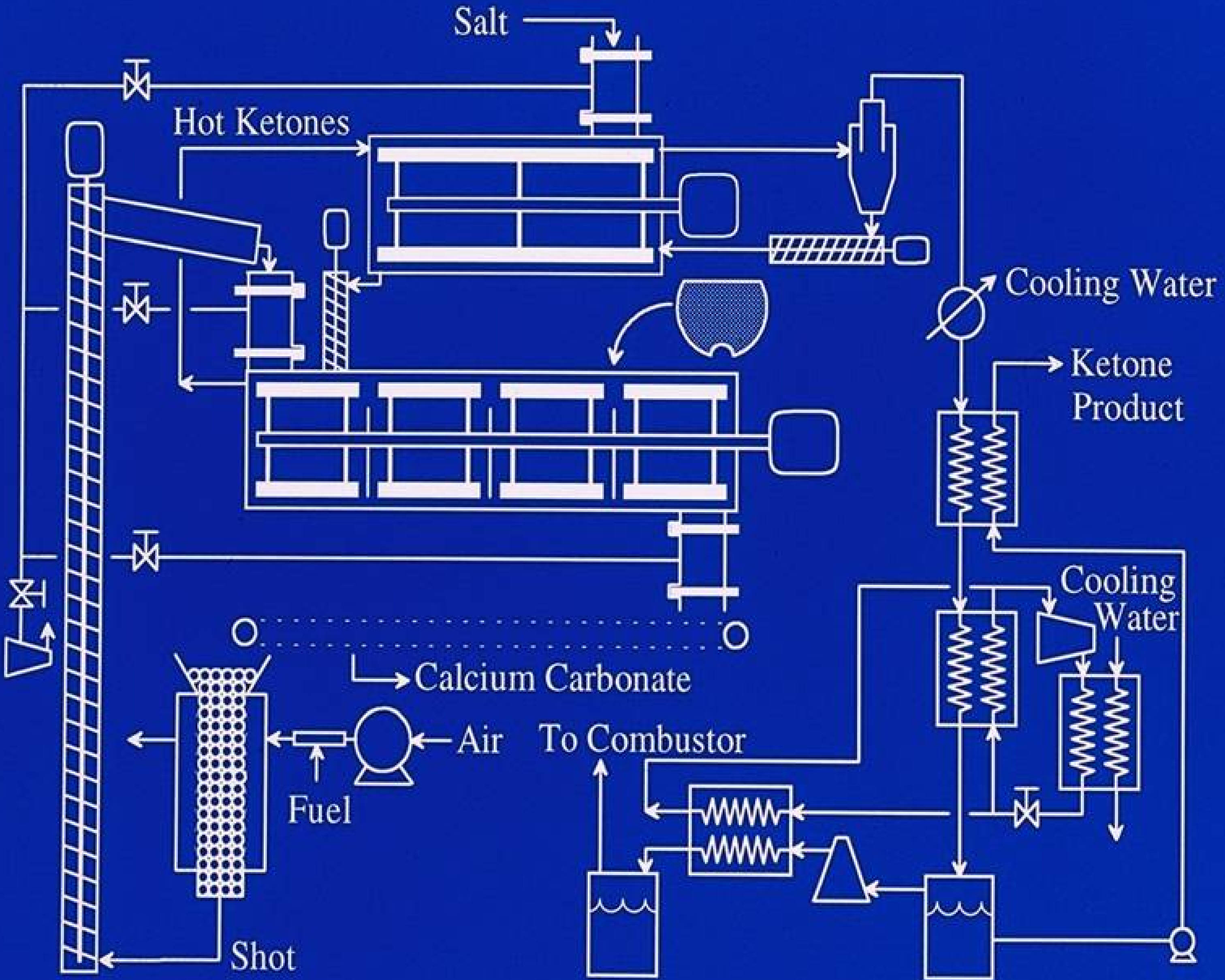
Thermal Conversion Stoichiometry

- Commonly known as dry distillation. Used before and during WWI to make acetone from calcium acetate

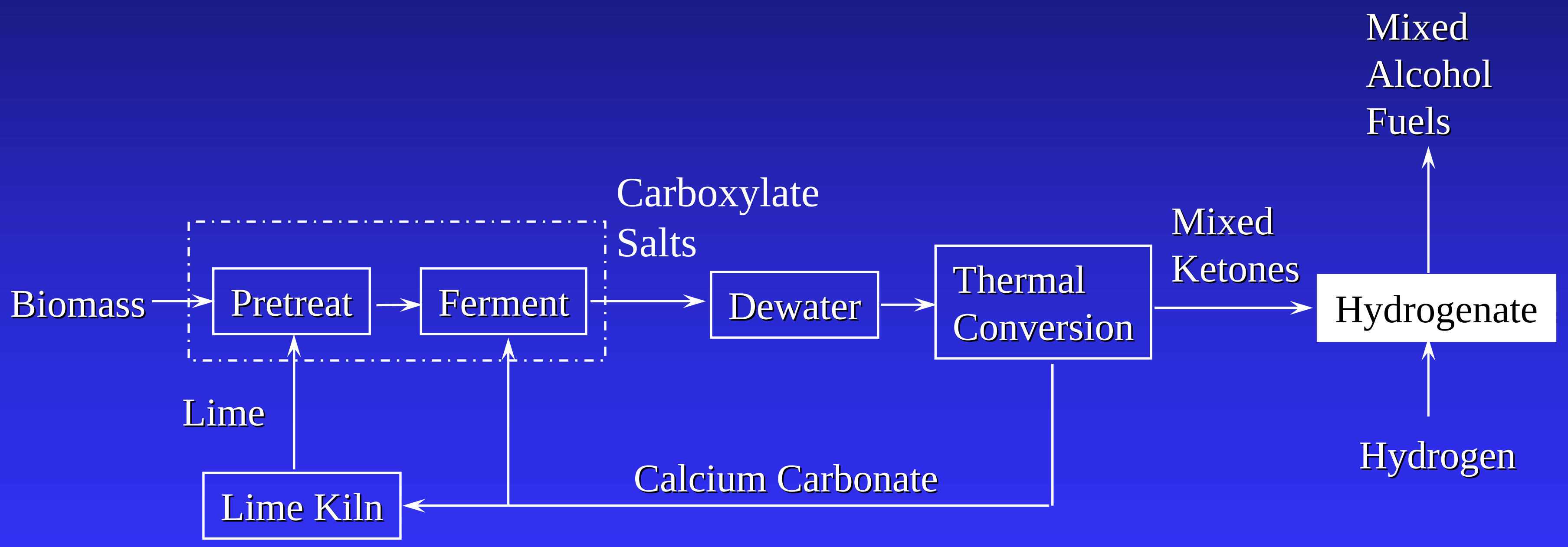
Thermal Conversion Kinetics



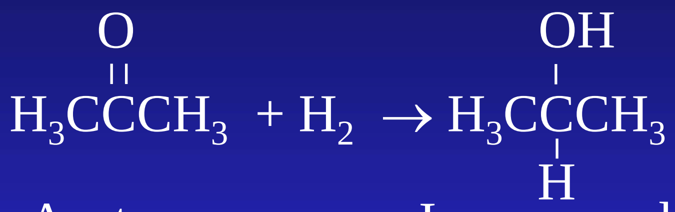
Thermal Conversion



Hydrogenation

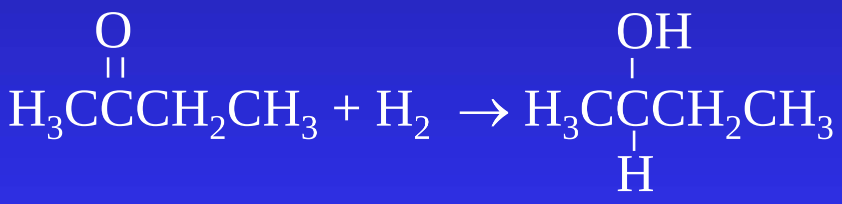


Ketone Hydrogenation Stoichiometry



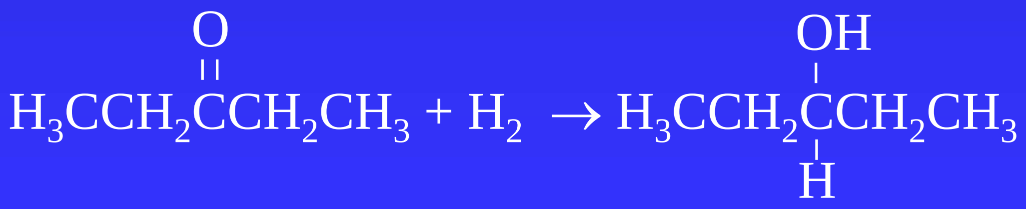
$$H_3C\overset{O}{\overset{\|}{C}}CH_3 + H_2 \rightarrow H_3C\overset{OH}{\underset{H}{C}}CH_3$$

Acetone Isopropanol



$$H_3C\overset{O}{\overset{\|}{C}}CH_2CH_3 + H_2 \rightarrow H_3C\overset{OH}{\underset{H}{C}}CH_2CH_3$$

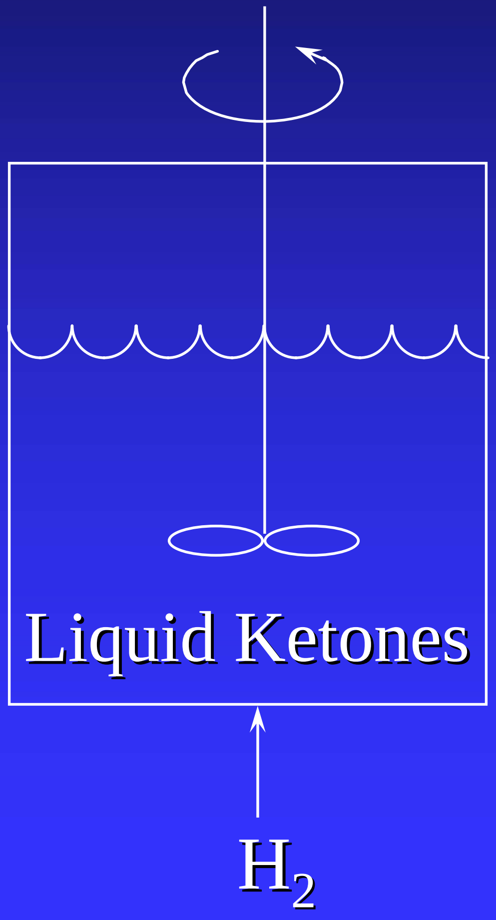
Methyl Ethyl Ketone 2-Butanol



$$H_3CCH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + H_2 \rightarrow H_3CCH_2\overset{OH}{\underset{H}{C}}CH_2CH_3$$

Diethyl Ketone 3-Pentanol

Ketone Hydrogenation

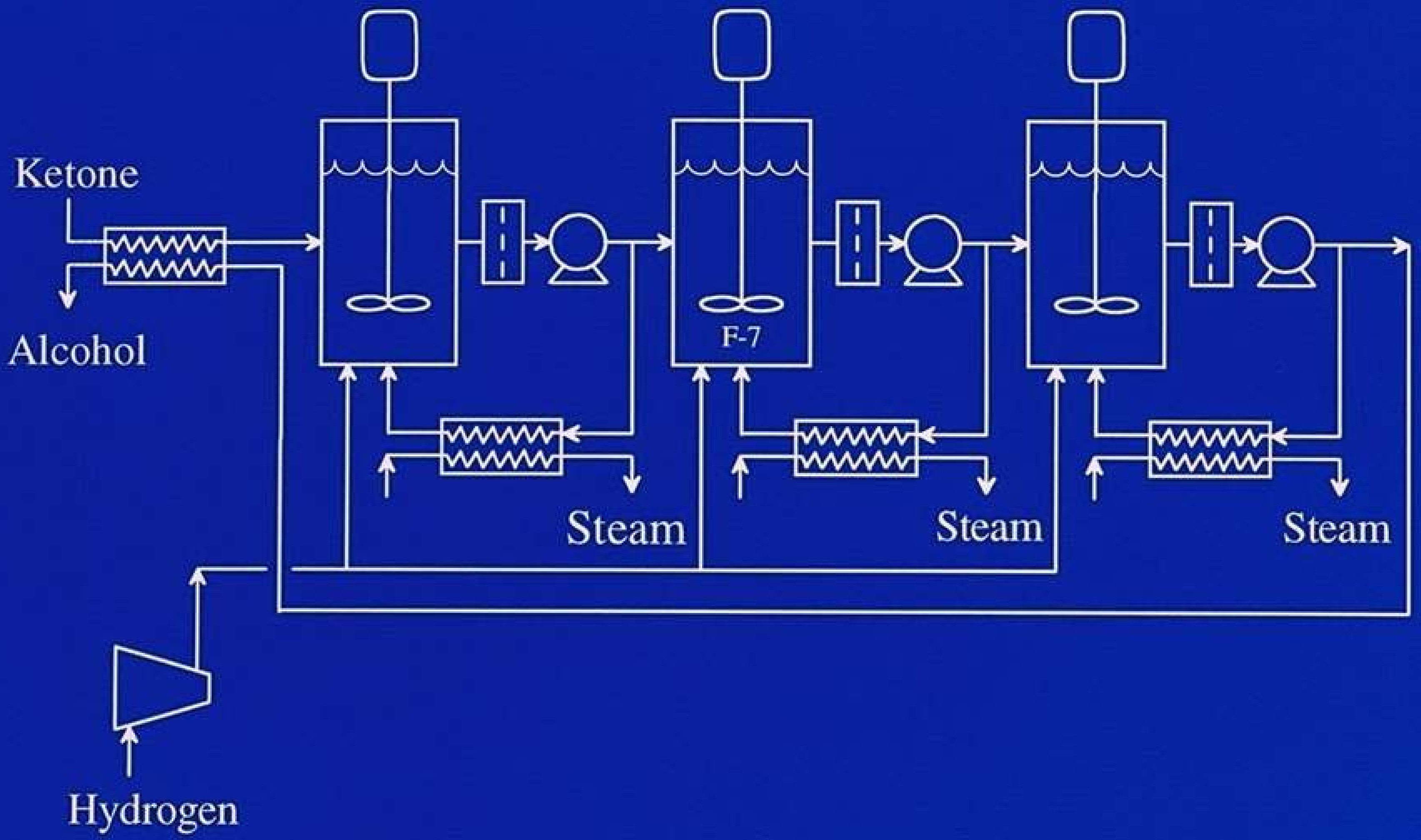


Catalyst = 200 g/L Raney nickel

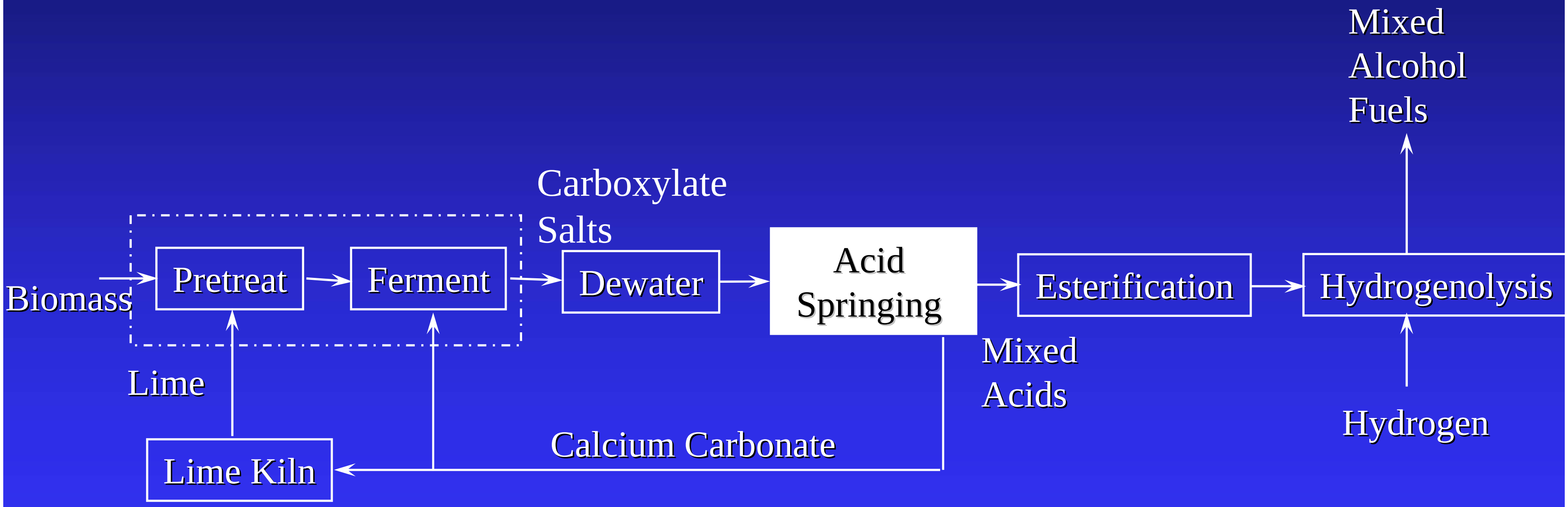
Temperature = 130°C

Time = 35 min
@ P = 15 atm (220 psi)

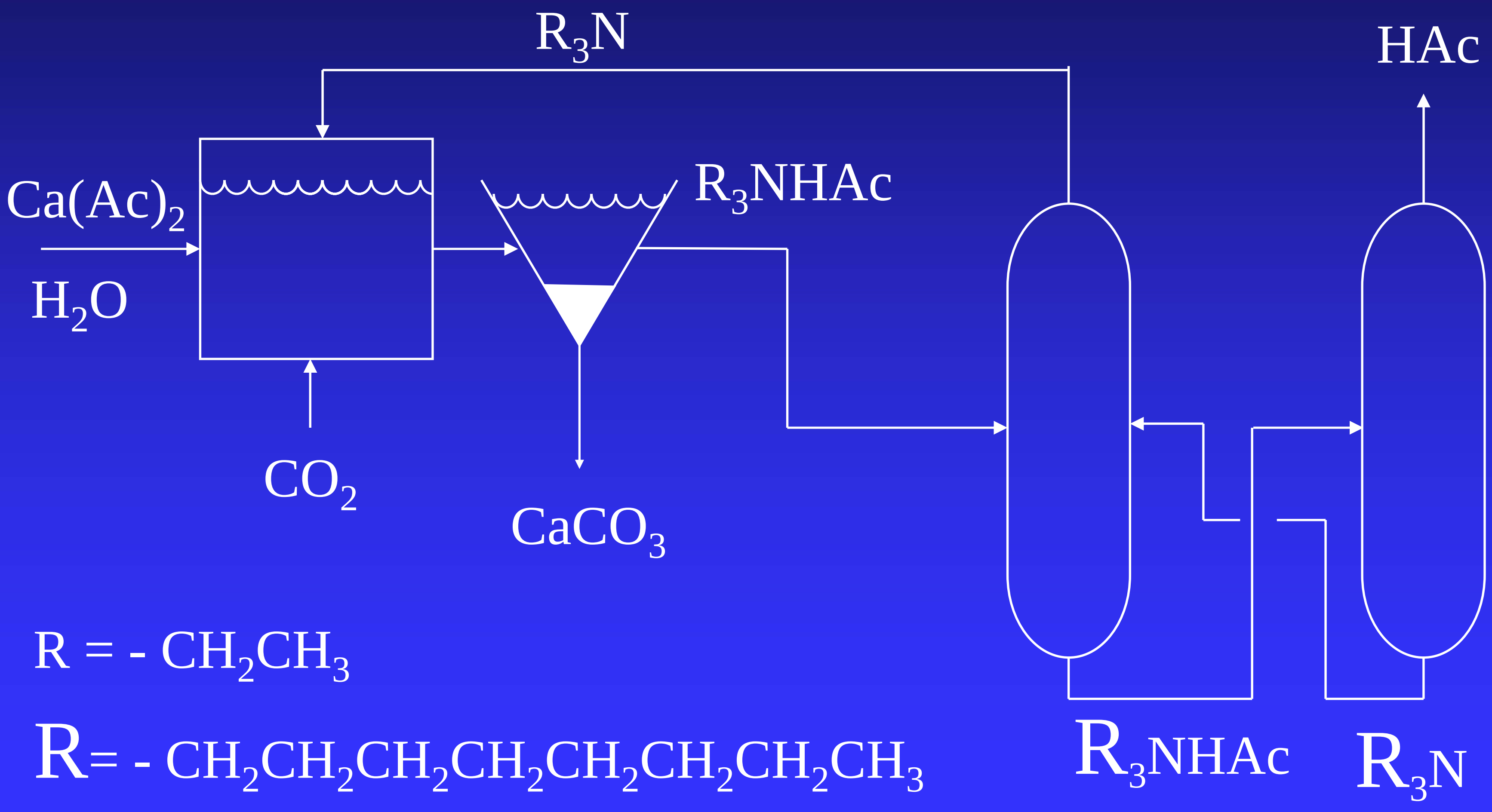
Hydrogenation



MixAlco Process – Version 2



Acid “Springing” Calcium Salts



R_3N

HAc

$Ca(Ac)_2$

H_2O

R_3NHAc

CO_2

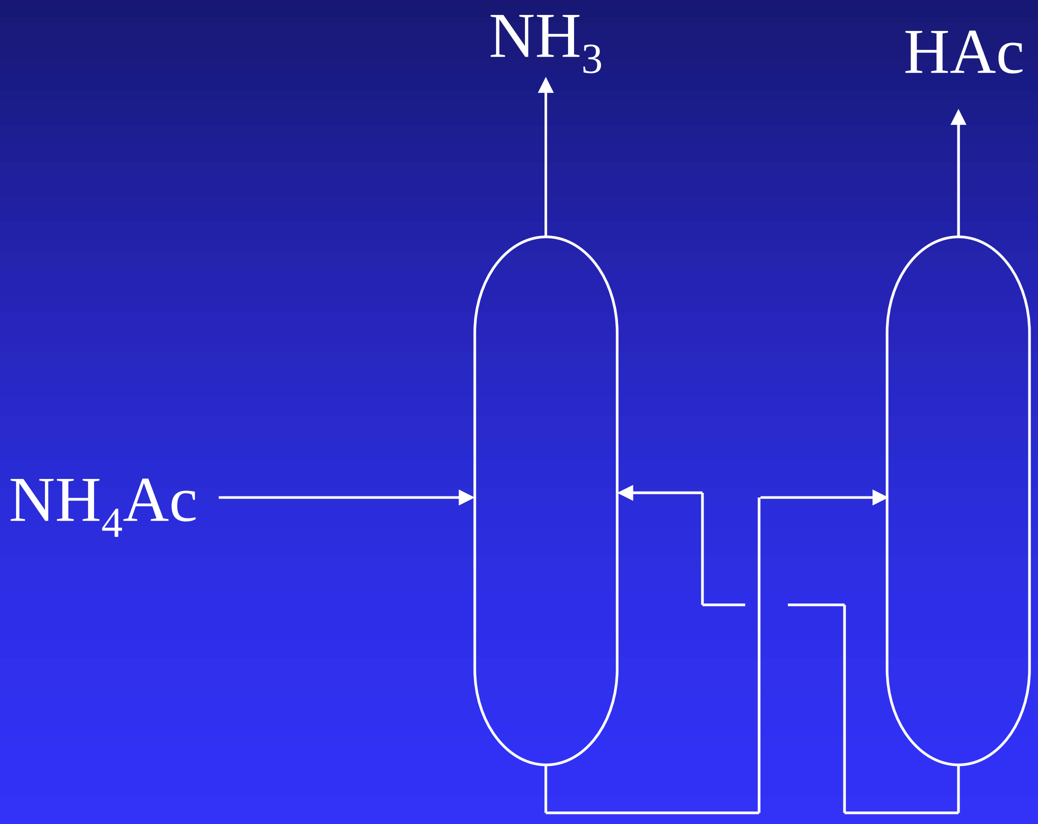
$CaCO_3$

R_3NHAc R_3N

$R = -CH_2CH_3$

$R = -CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Acid "Springing" Ammonium Salts



NH_3

HAc

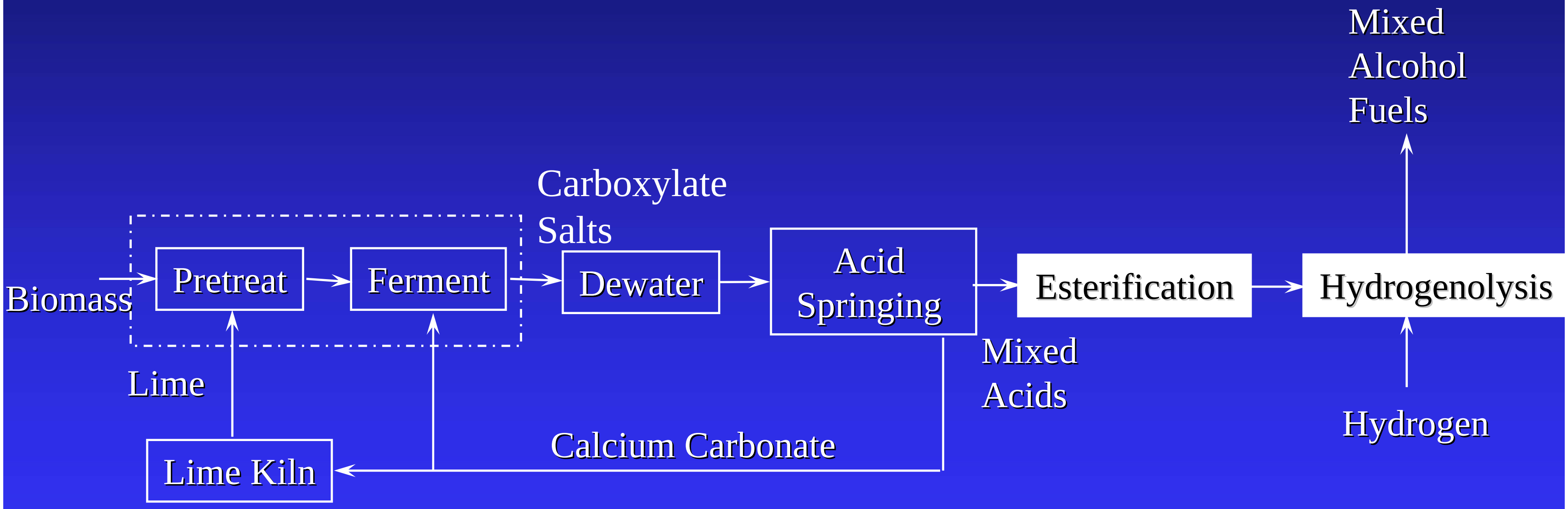
NH_4Ac

R_3NHAc

R_3N

$R = -CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

MixAlco Process – Version 2



Mixed Alcohol Fuels

Carboxylate Salts

Biomass

Pretreat

Ferment

Dewater

Acid Springing

Esterification

Hydrogenolysis

Mixed Acids

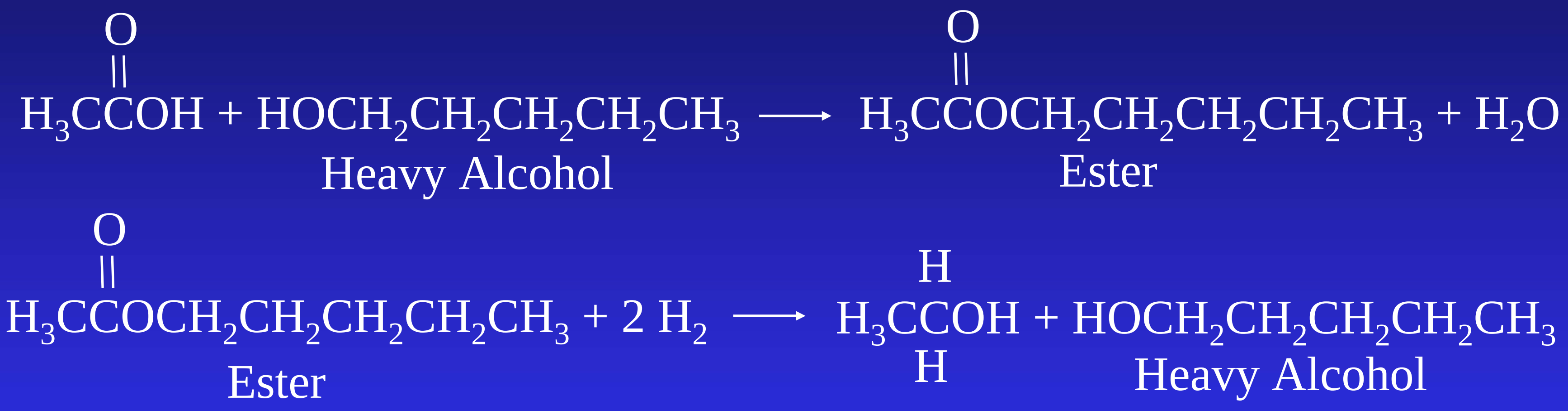
Lime

Hydrogen

Calcium Carbonate

Lime Kiln

Hydrogenation Stoichiometry



$$H_3C\overset{\overset{O}{\|}}{C}OH + HOCH_2CH_2CH_2CH_2CH_3 \longrightarrow H_3C\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_2CH_2CH_3 + H_2O$$

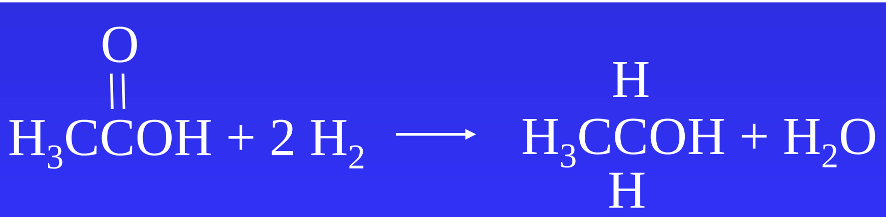
Heavy Alcohol

Ester

$$H_3C\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_2CH_2CH_3 + 2\,H_2 \longrightarrow H_3C\underset{H}{\overset{H}{C}}OH + HOCH_2CH_2CH_2CH_2CH_3$$

Ester

Heavy Alcohol

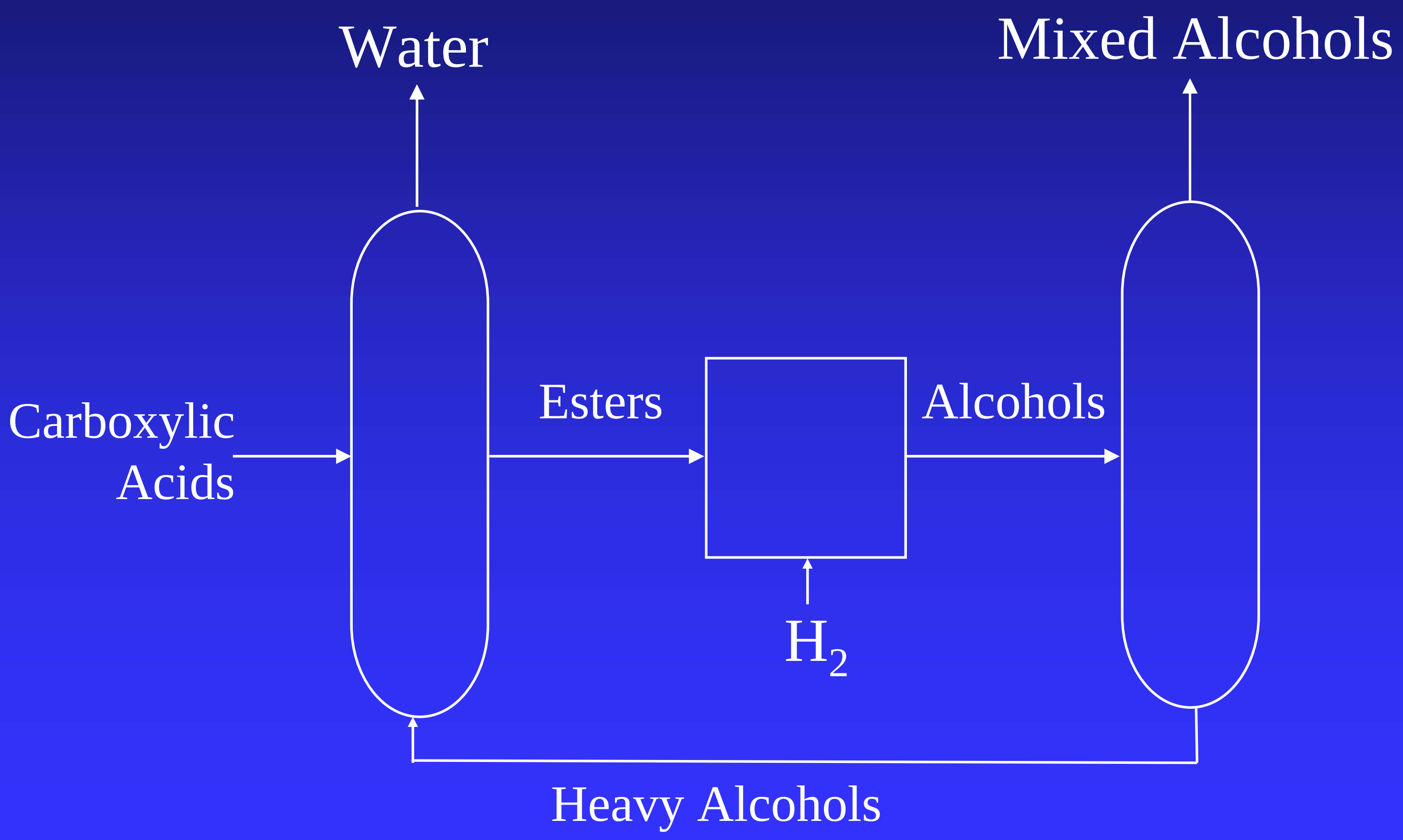


$$H_3C\overset{\overset{O}{\|}}{C}OH + 2\,H_2 \longrightarrow H_3C\underset{H}{\overset{H}{C}}OH + H_2O$$

Acetic Acid

Ethanol

Esterification + Hydrogenolysis



Water

Mixed Alcohols

Carboxylic Acids

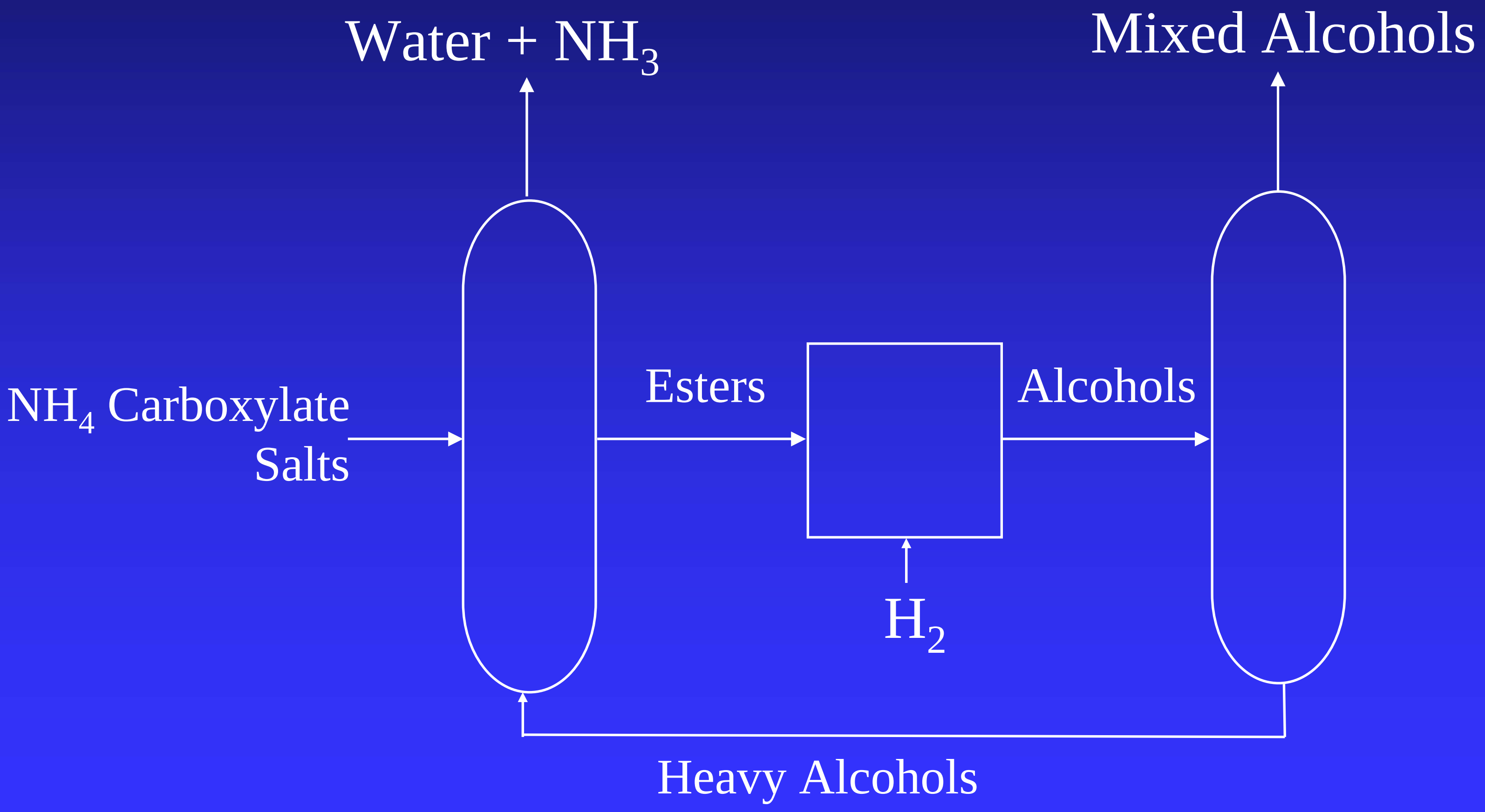
Esters

Alcohols

H_2

Heavy Alcohols

Esterification + Hydrogenolysis



Water + NH_3

Mixed Alcohols

NH_4 Carboxylate Salts

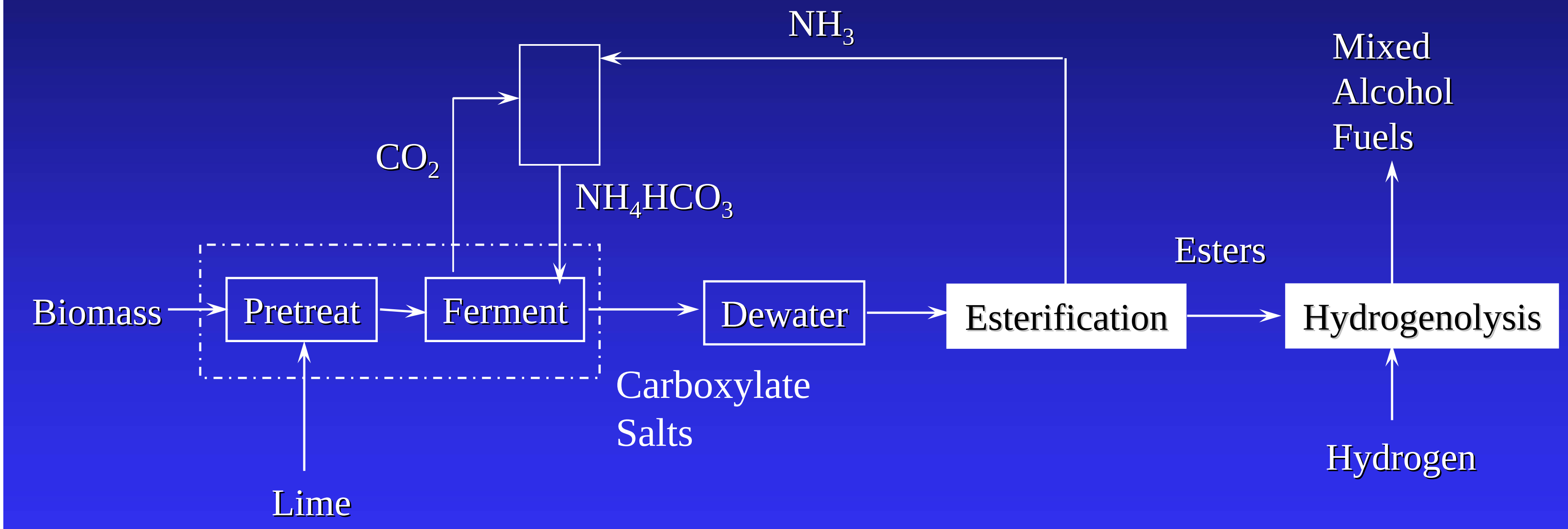
Esters

Alcohols

H_2

Heavy Alcohols

MixAlco Process – Version 2
Ammonium Salts



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^{o}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^{o}C)
  - low pressure (<350 psi)
  - preferred

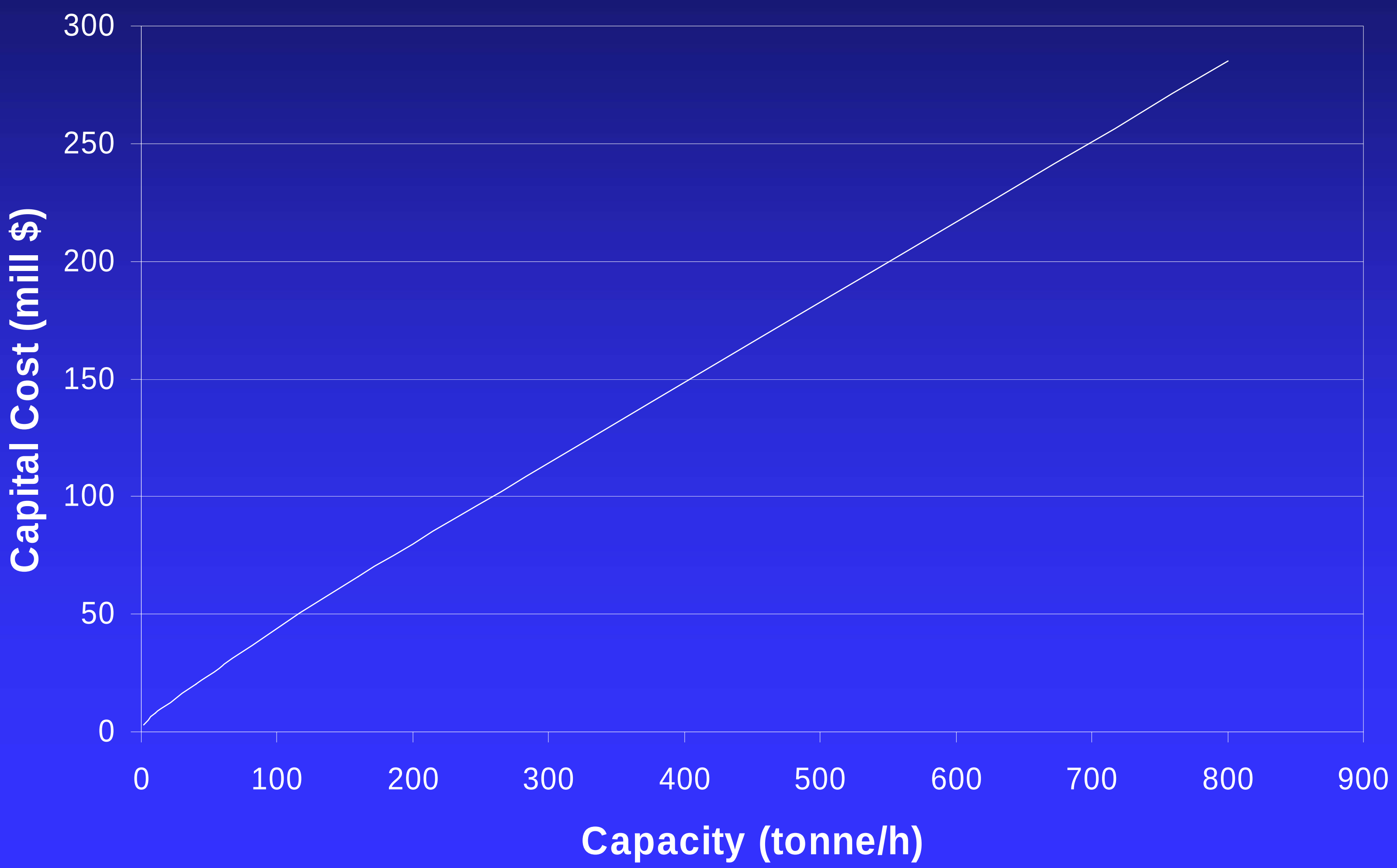
Economics

Plant Capacity

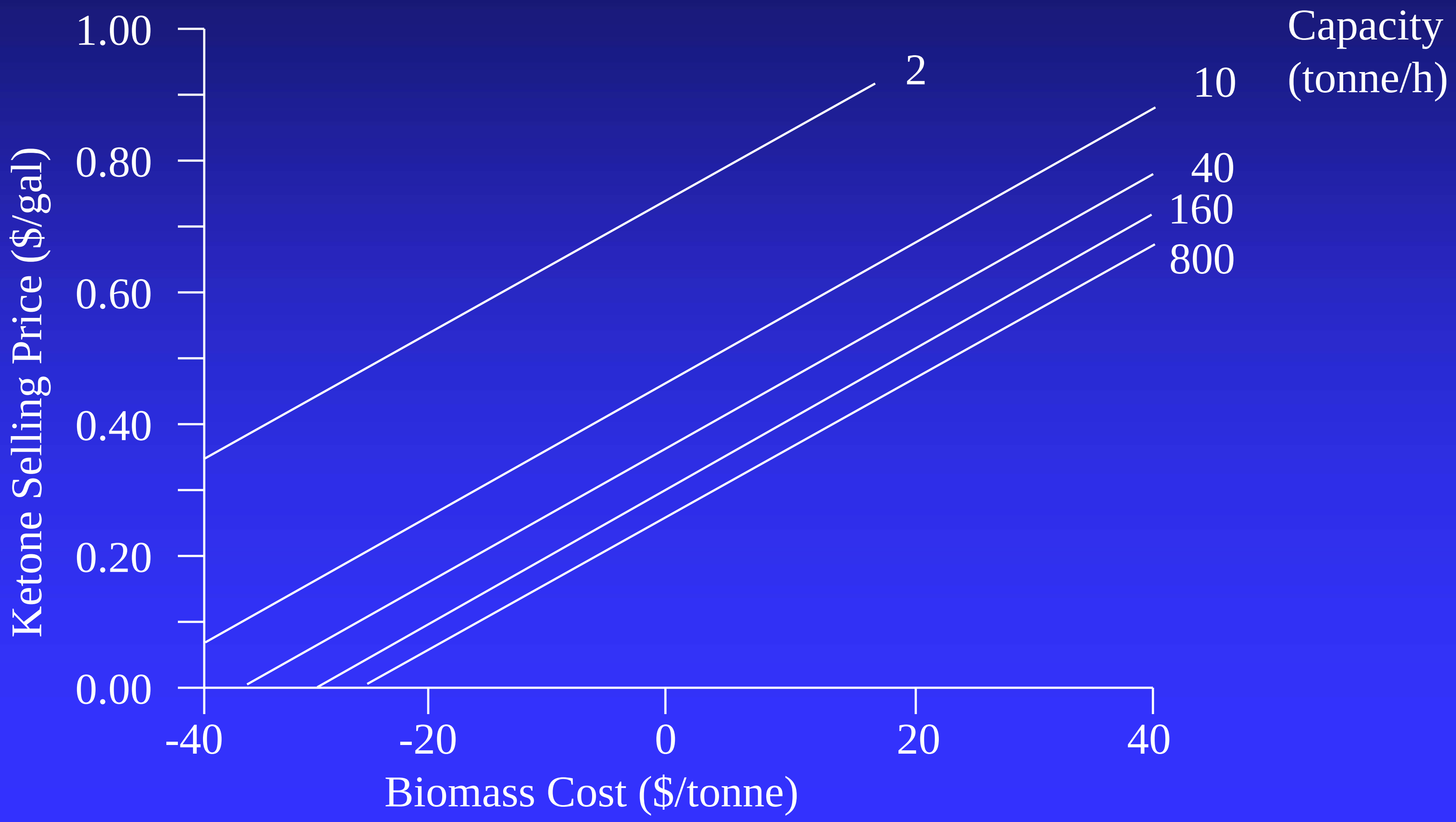
	Plant Capacity			*City Population
	(tonne/h)	(mill gal/yr)		
		Version 1	Version 2	
	2	1.5	2.3	40,000
	10	7.6	11.3	200,000
Base Case →	40	30.3	45.1	800,000
	160	121	181	3,200,000
	800	606	903	16,000,000

* Feedstock = Municipal solid waste + Sewage sludge

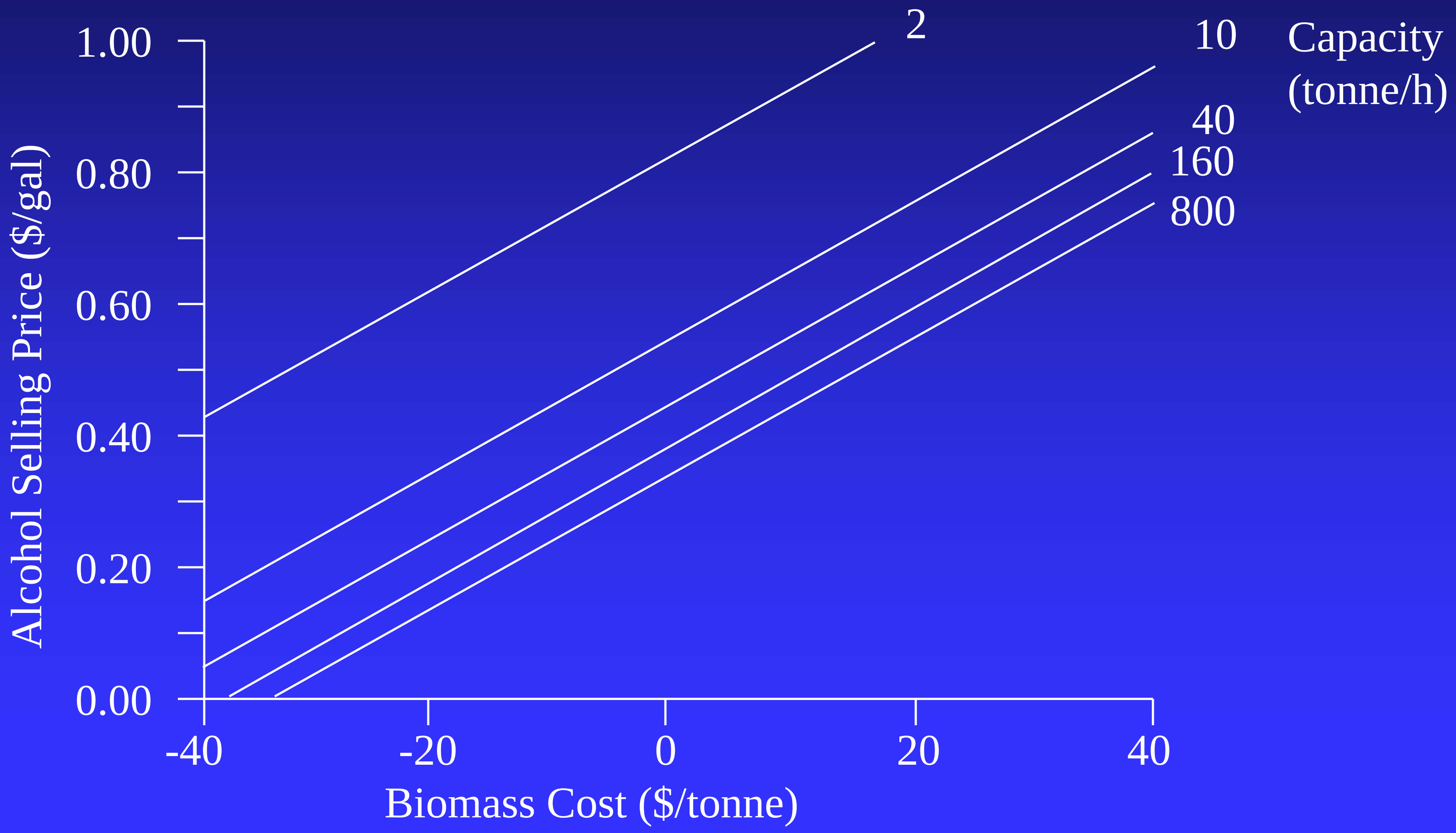
Effect of Scale on Capital Cost –Versions 1&2



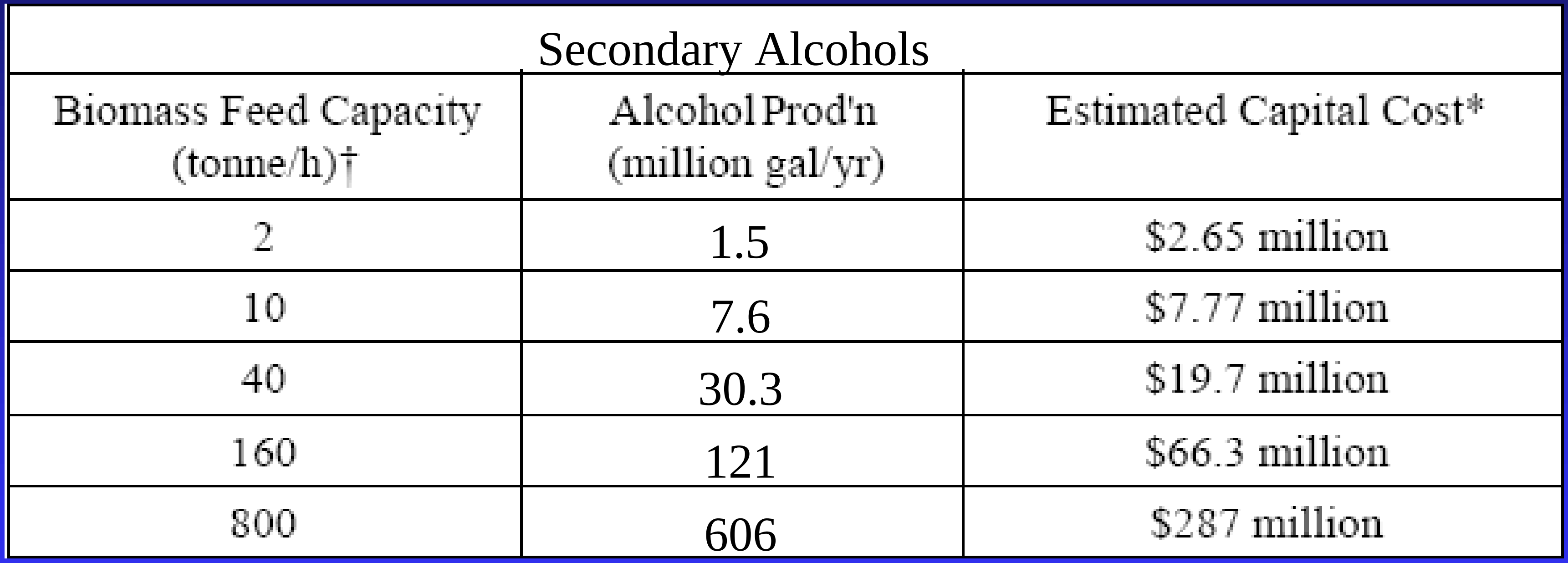
Mixed Ketone Selling Price
Version 1 (15% ROI)



Mixed Alcohol Selling Price Version 1 (15% ROI)



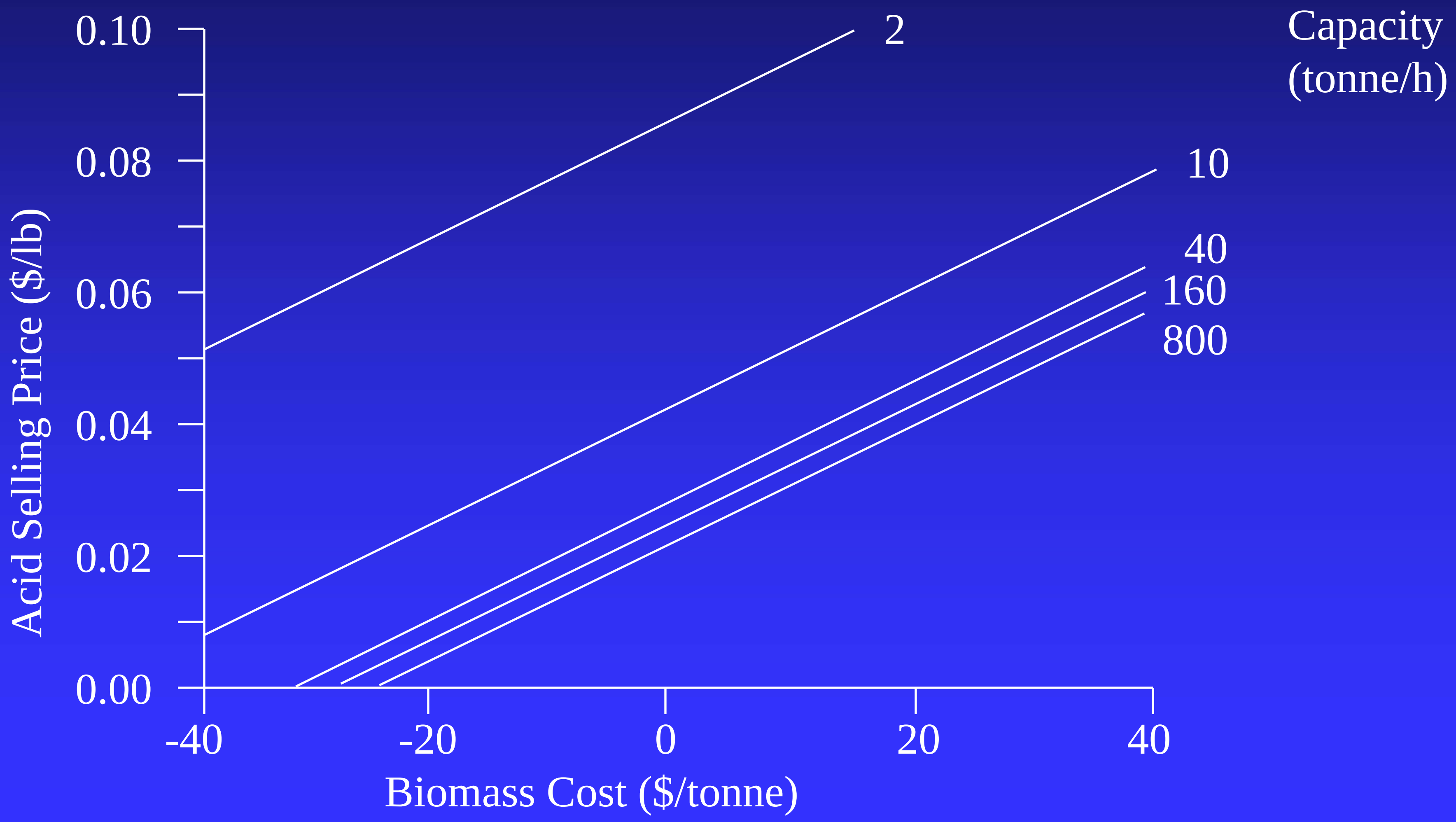
Mixed Secondary Alcohols (e.g., isopropanol) (Version 1)



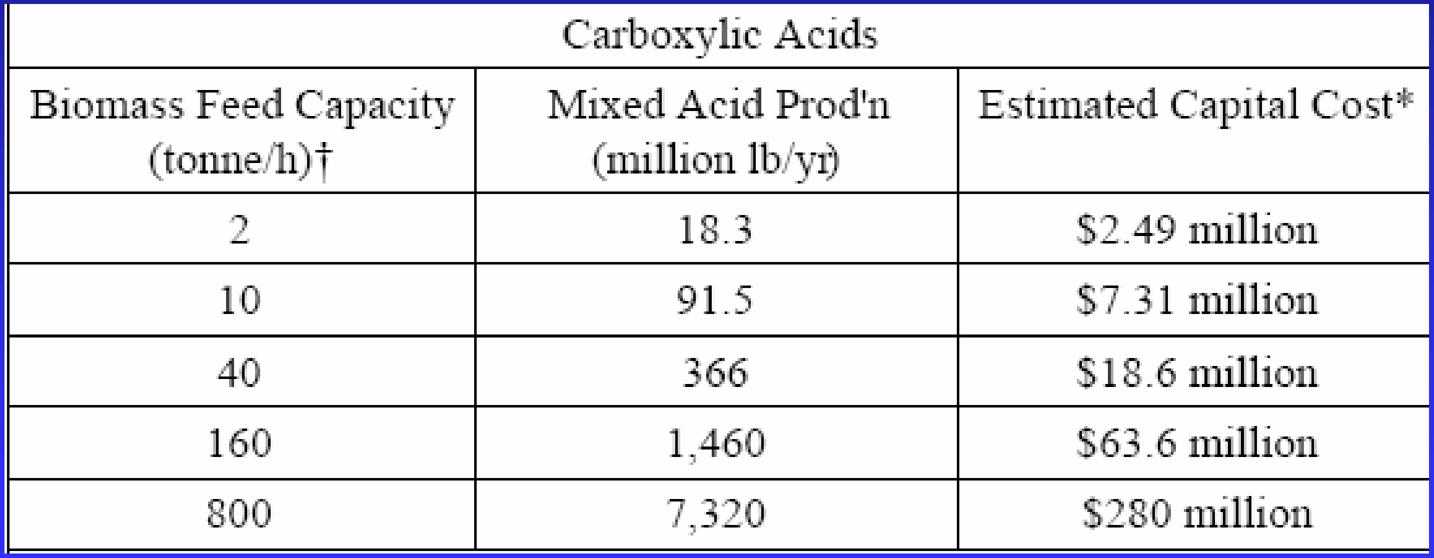
Secondary Alcohols		
Biomass Feed Capacity (tonne/h)†	Alcohol Prod'n (million gal/yr)	Estimated Capital Cost*
2	1.5	$2.65 million
10	7.6	$7.77 million
40	30.3	$19.7 million
160	121	$66.3 million
800	606	$287 million

Yield = ~ 86 gal/dry ton

Mixed Acid Selling Price
Version 2 (15% ROI)



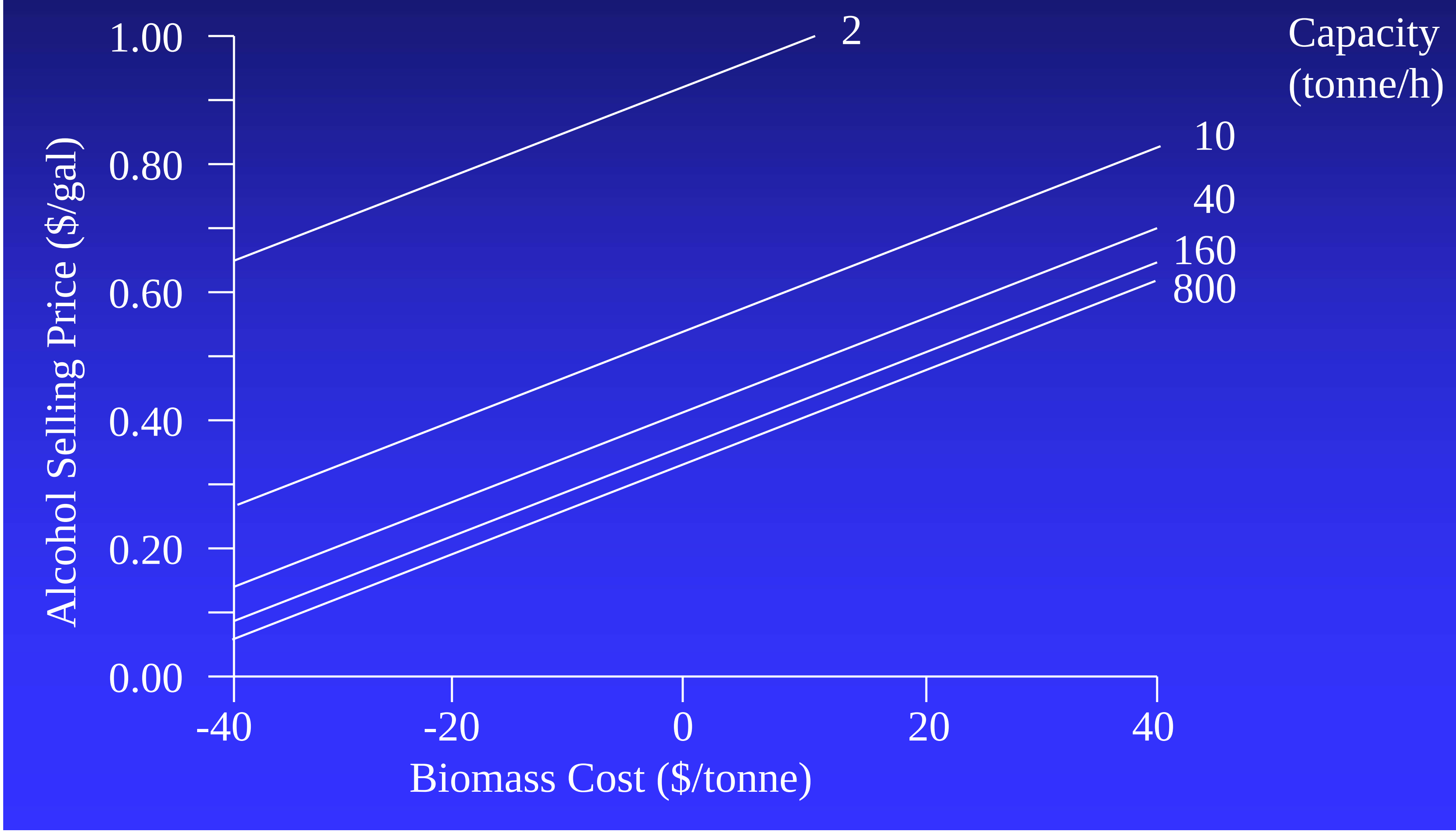
Carboxylic Acids



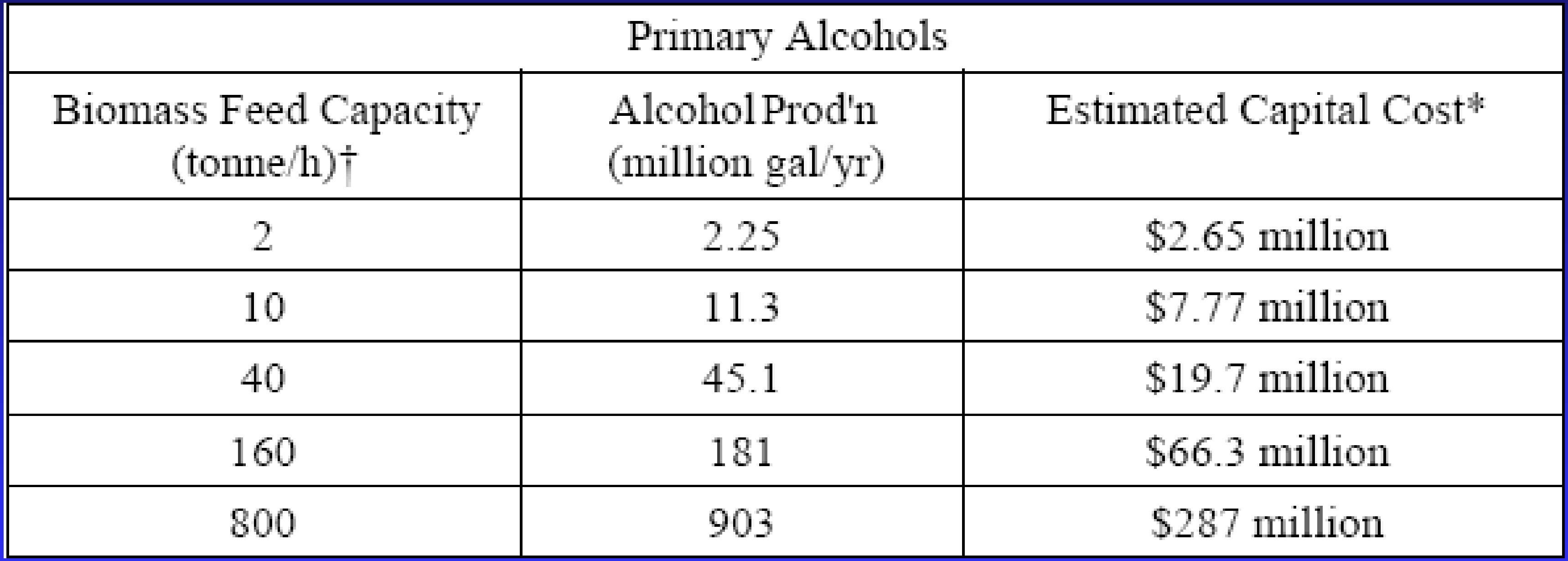
Carboxylic Acids		
Biomass Feed Capacity (tonne/h)†	Mixed Acid Prod'n (million lb/yr)	Estimated Capital Cost*
2	18.3	$2.49 million
10	91.5	$7.31 million
40	366	$18.6 million
160	1,460	$63.6 million
800	7,320	$280 million

Mixed Alcohol Selling Price Version 2

(15% ROI)



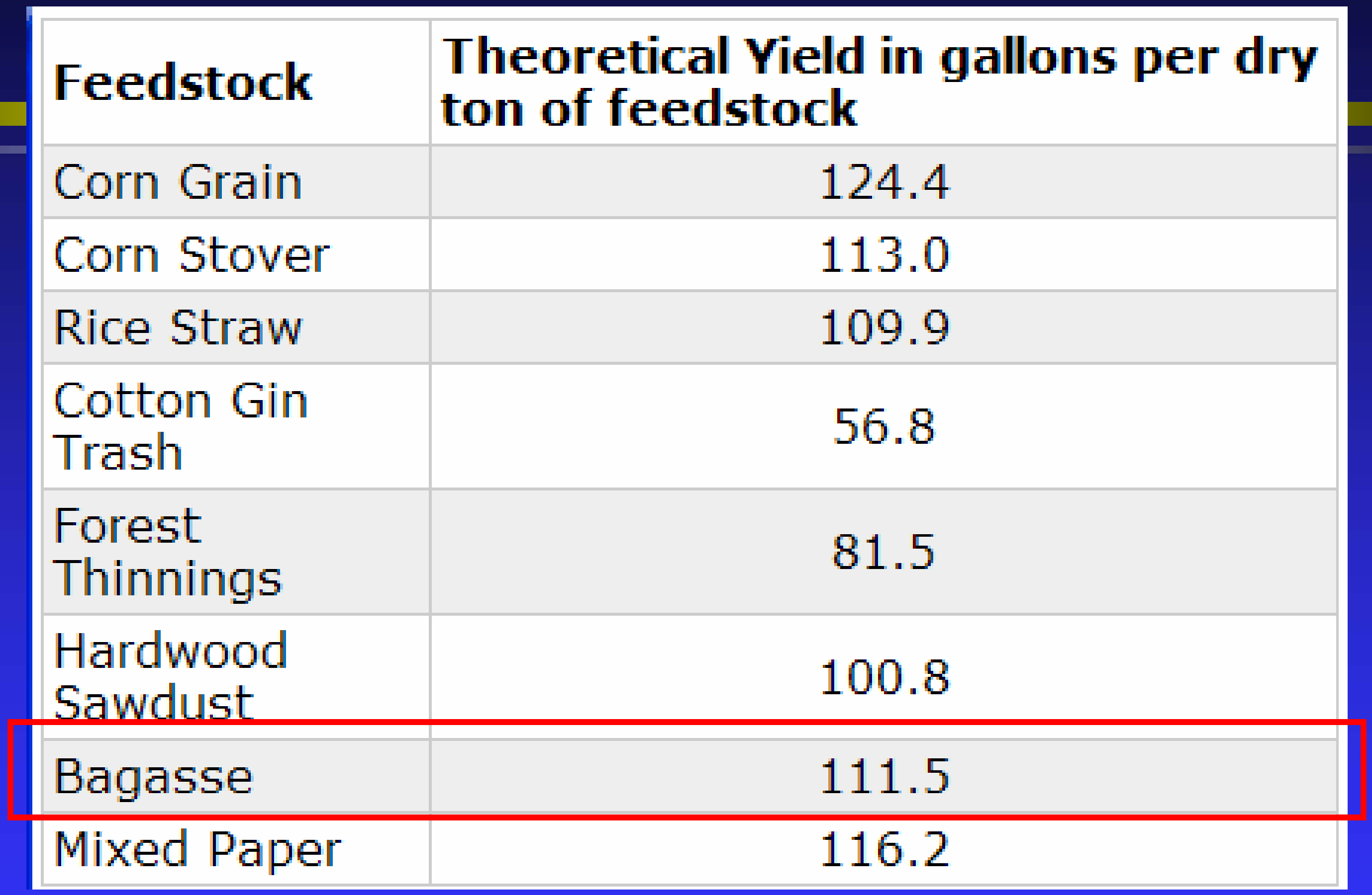
Mixed Primary Alcohols (e.g., ethanol) (Version 2)



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

Yield = ~ 130 gal/dry ton

Enzymatic route/ethanol fermentation



Feedstock	Theoretical Yield in gallons per dry ton of feedstock
Corn Grain	124.4
Corn Stover	113.0
Rice Straw	109.9
Cotton Gin Trash	56.8
Forest Thinnings	81.5
Hardwood Sawdust	100.8
Bagasse	111.5
Mixed Paper	116.2

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

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

Energy Content

	Energy	
	(MJ/L)	(Btu/gal)
Gasoline	34.9	125,000
Mixed Alcohols Version 1	29.0	104,000
Mixed Alcohols Version 2	26.5	95,000
Ethanol	23.4	84,300

Yield on an ethanol equivalent basis

$$130 \text{ gal/ton } \times 95{,}000/84{,}300 = \boxed{147 \text{ gal/ton}}$$

~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

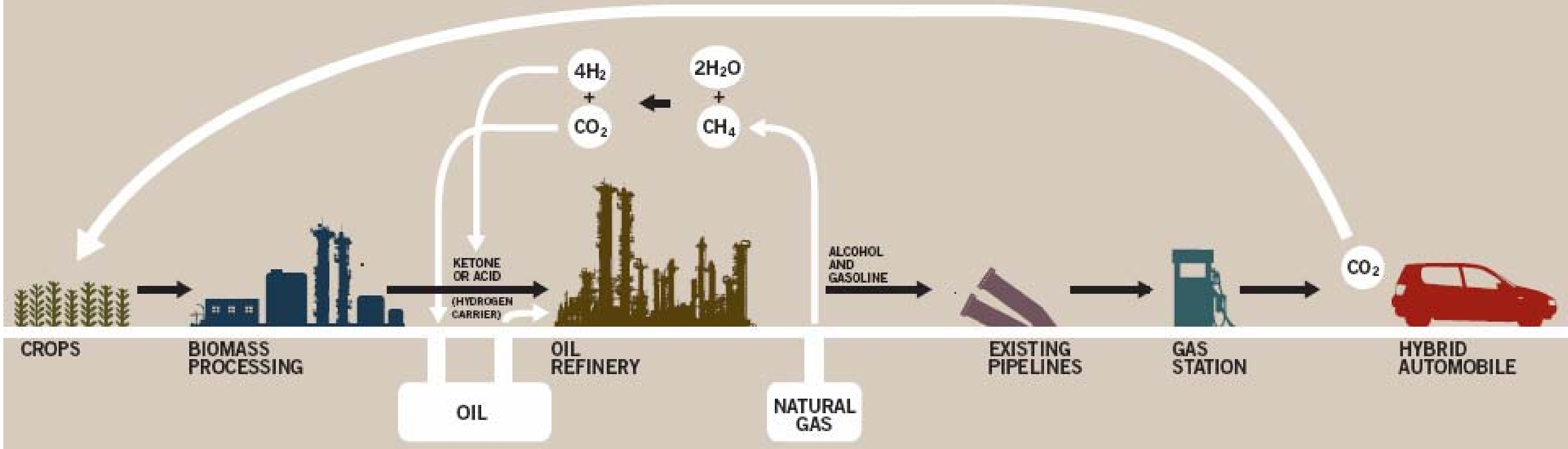
  - waste → chemicals

- Mid-term applications

  - waste → fuels

- Far-term applications

  - crops → fuels



Thank you for your time and attention