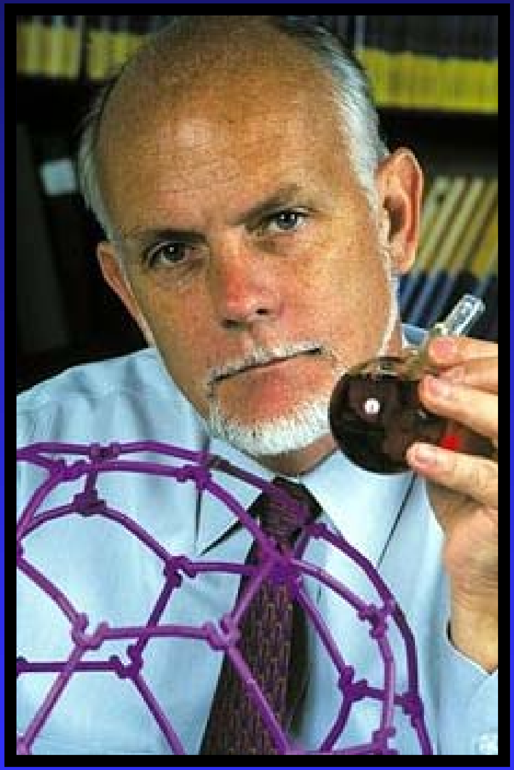
Richard Smalley



1943 to 2005

Nobel Prize in Chemistry in 1996

“Buckeyballs”

Smalley's Top Ten Human Problems

1. Energy
2. Water
3. Food
4. Environment
5. Poverty
6. Terrorism/War
7. Disease
8. Education
9. Democracy
10. Population

http://cohesion.rice.edu/NaturalSciences/Smalley/emplibrary/120204%20MRS%20Boston.pdf

Smalley’s Bold Claim

All of these problems can be addressed with energy that is

- Clean
- Affordable
- Abundant

Smalley's Top Ten Human Problems

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http://cohesion.rice.edu/NaturalSciences/Smalley/emplibrary/120204%20MRS%20Boston.pdf

Smalley's Top Ten Human Problems

1. Energy
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7. Energy
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9. Energy
10. Energy

http://cohesion.rice.edu/NaturalSciences/Smalley/emplibrary/120204%20MRS%20Boston.pdf

Energy

Mark Holtzapple
Department of Chemical Engineering
Texas A&M
College Station, TX

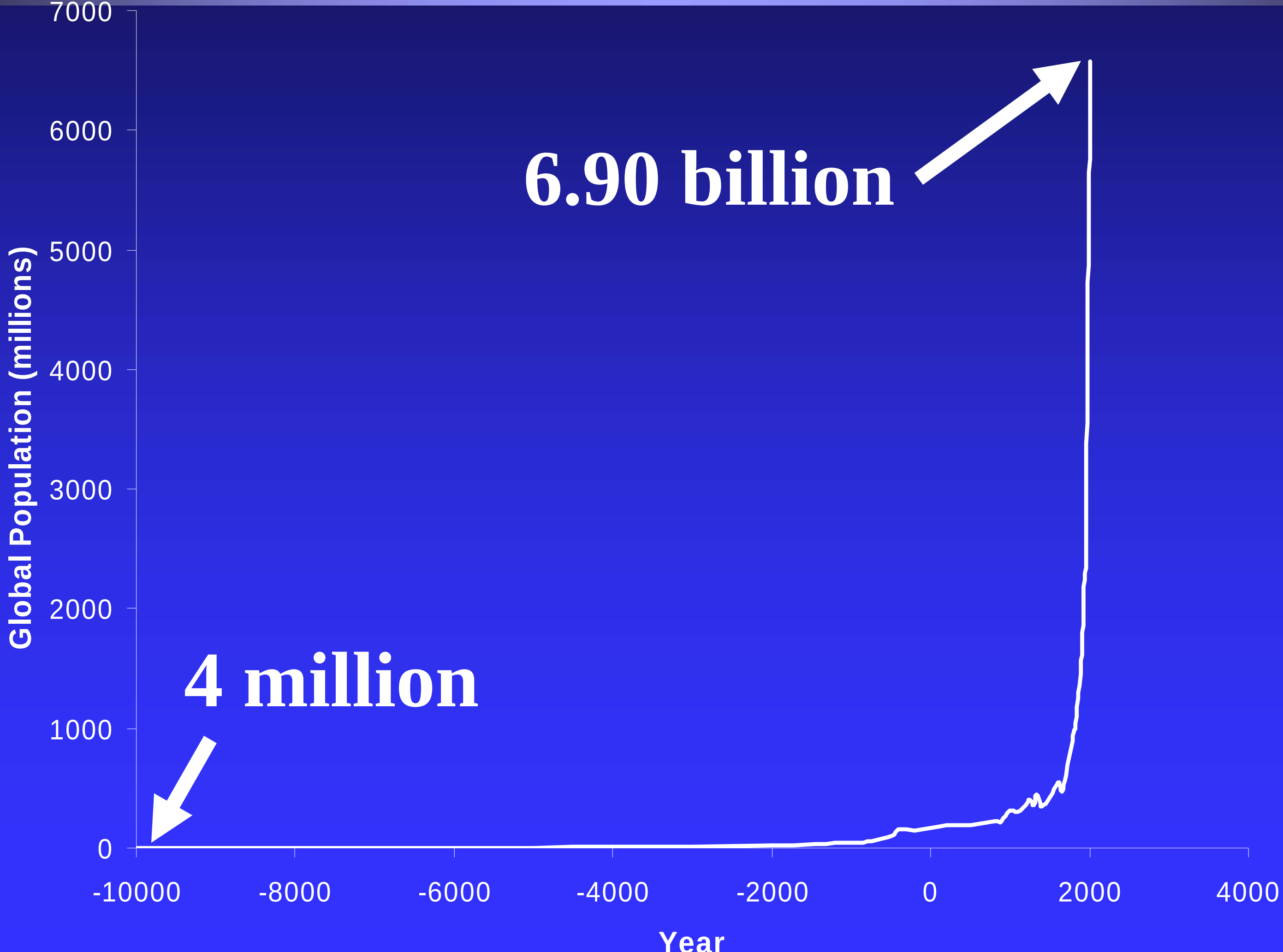
Outline

- Background
- Biofuels
- Advanced Engines

Driving Forces

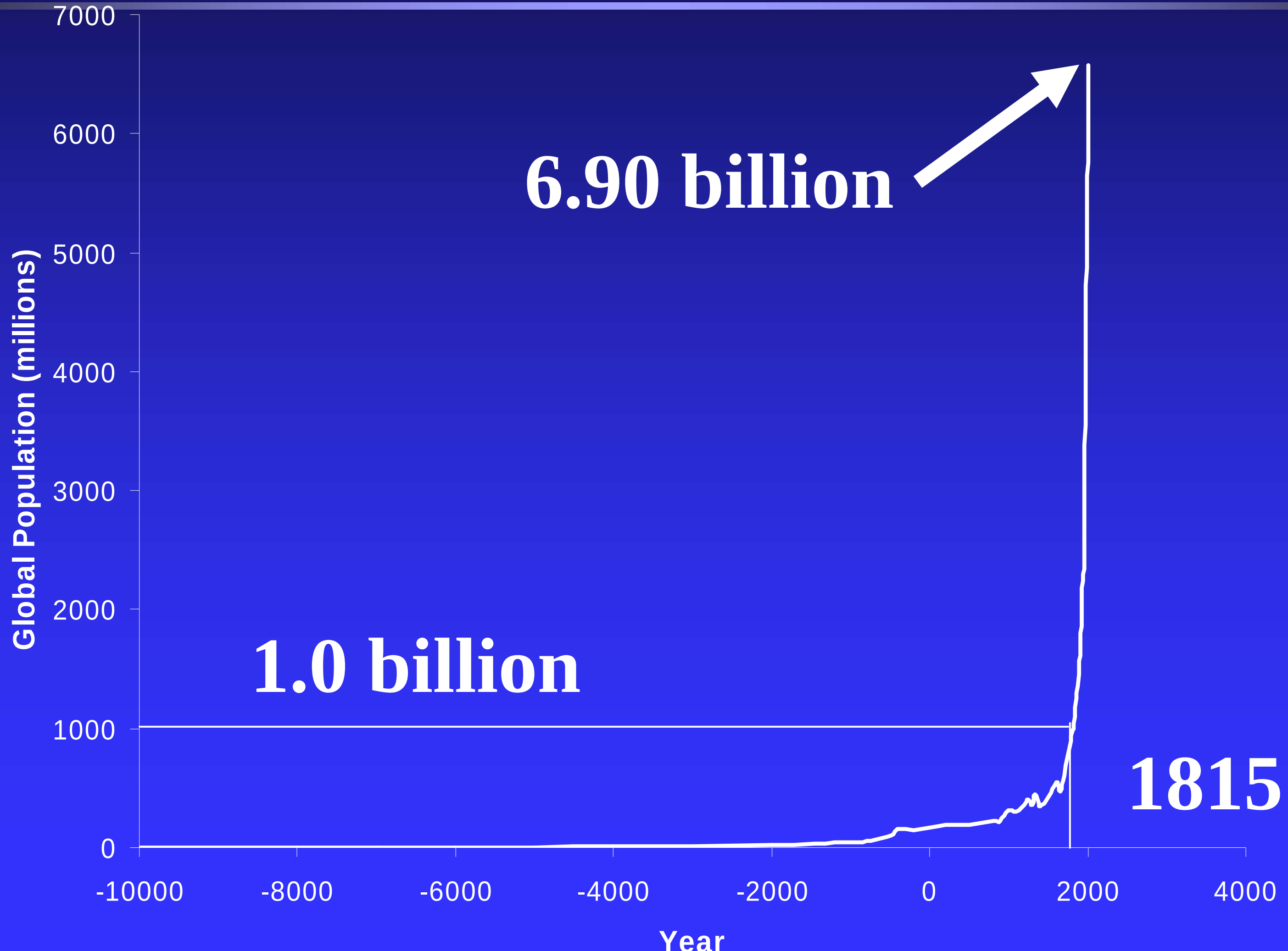
- Growing population
- Rising standard of living
- Oil imports
- Peak oil
- Global warming

Global Population



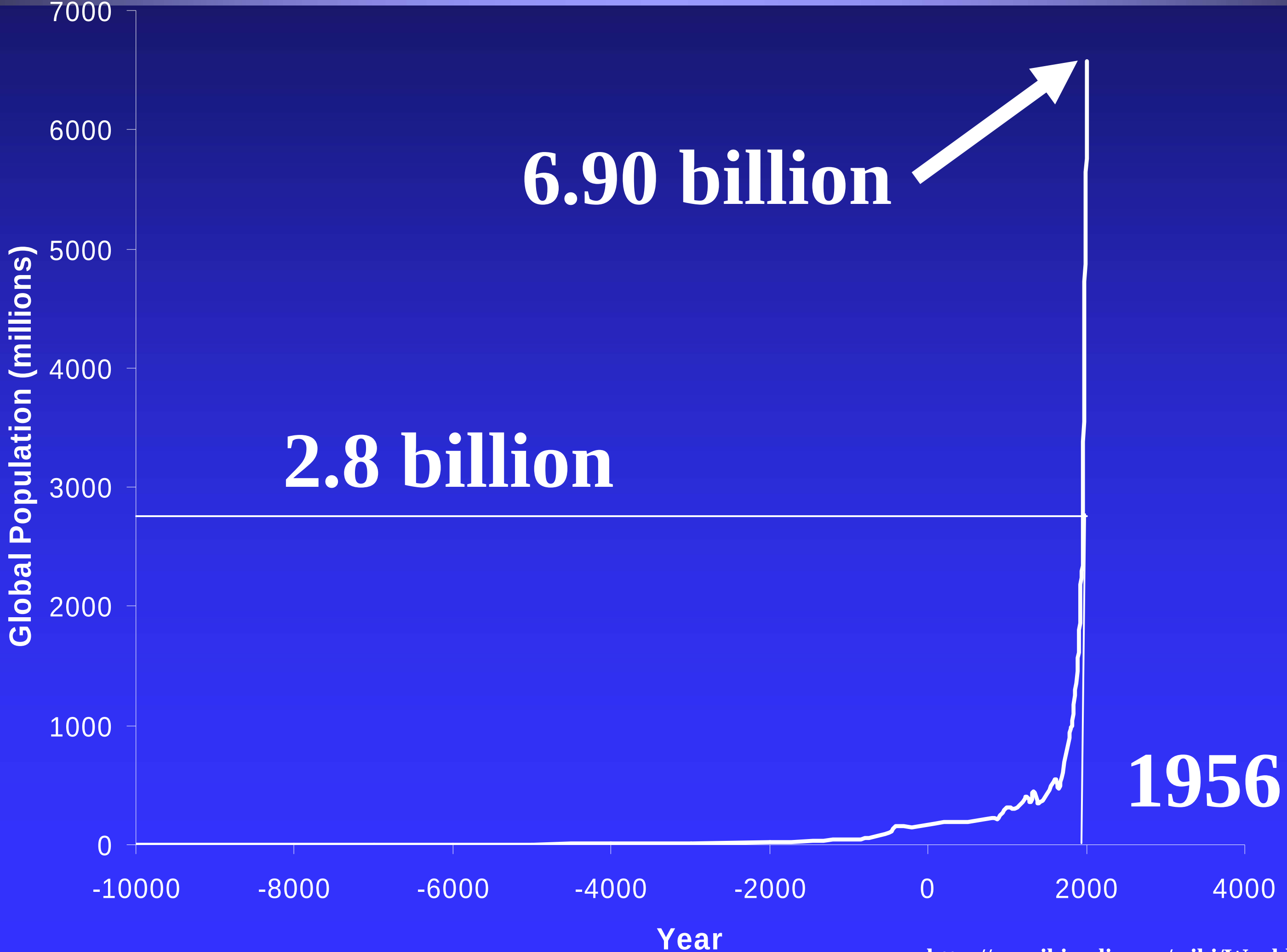
http://en.wikipedia.org/wiki/World_population

Global Population Milestones



http://en.wikipedia.org/wiki/World_population

Global Population Milestones



http://en.wikipedia.org/wiki/World_population

Driving Forces

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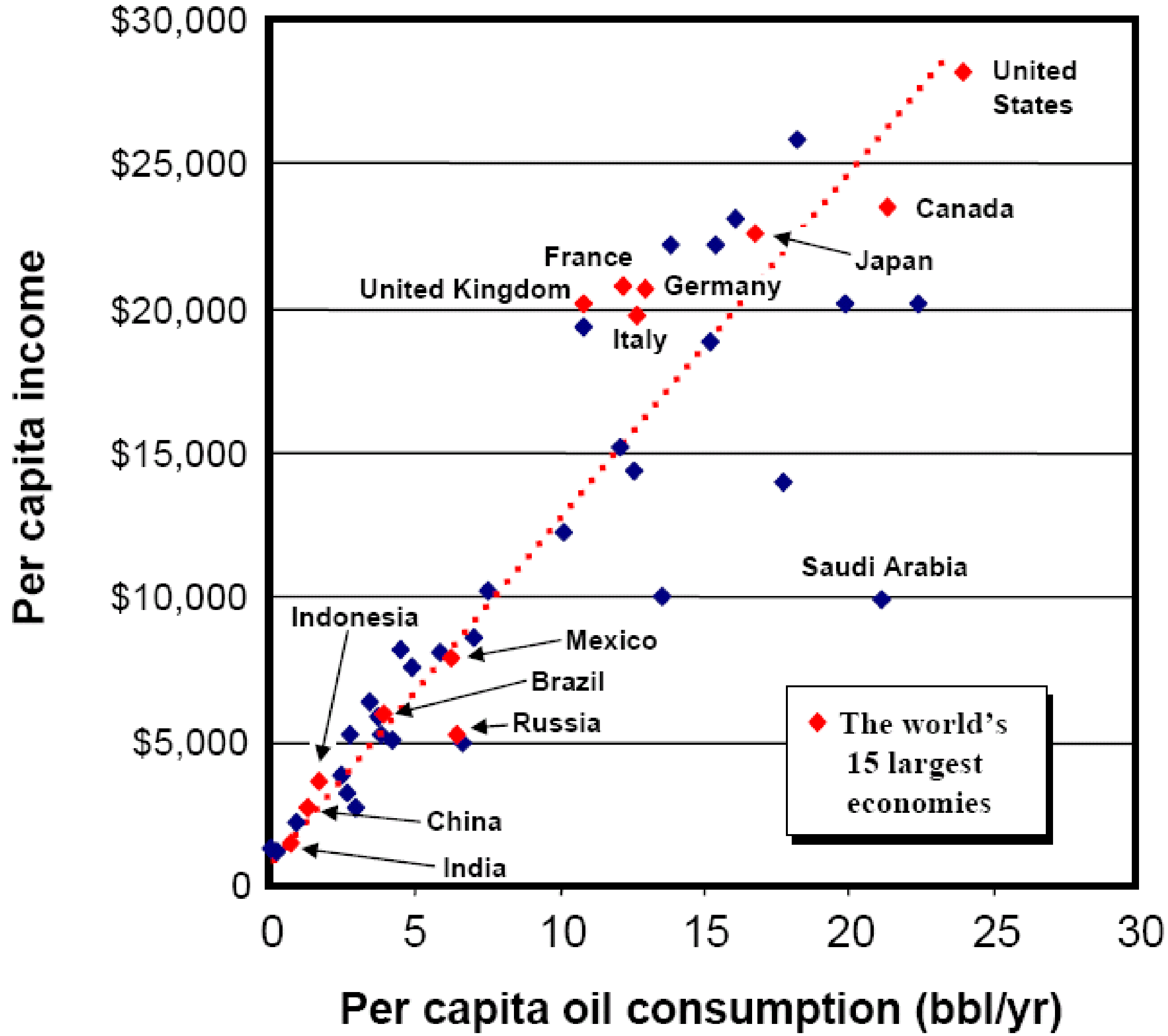
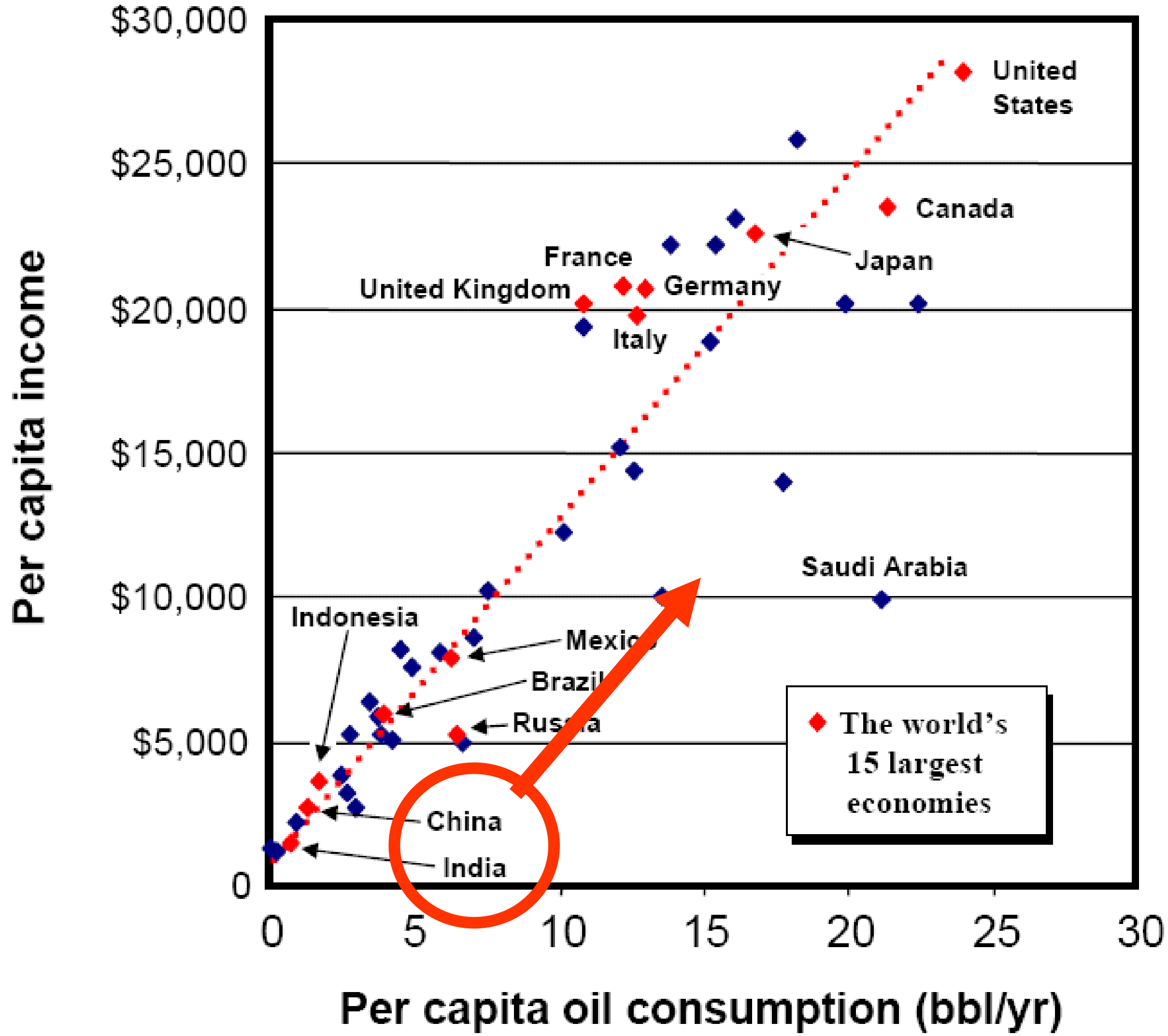
Big Picture

Energy and Wealth



Source: Economides and Oligney: *The Color of Oil*

Energy and Wealth



Source: Economides and Oligney: *The Color of Oil*

Driving Forces

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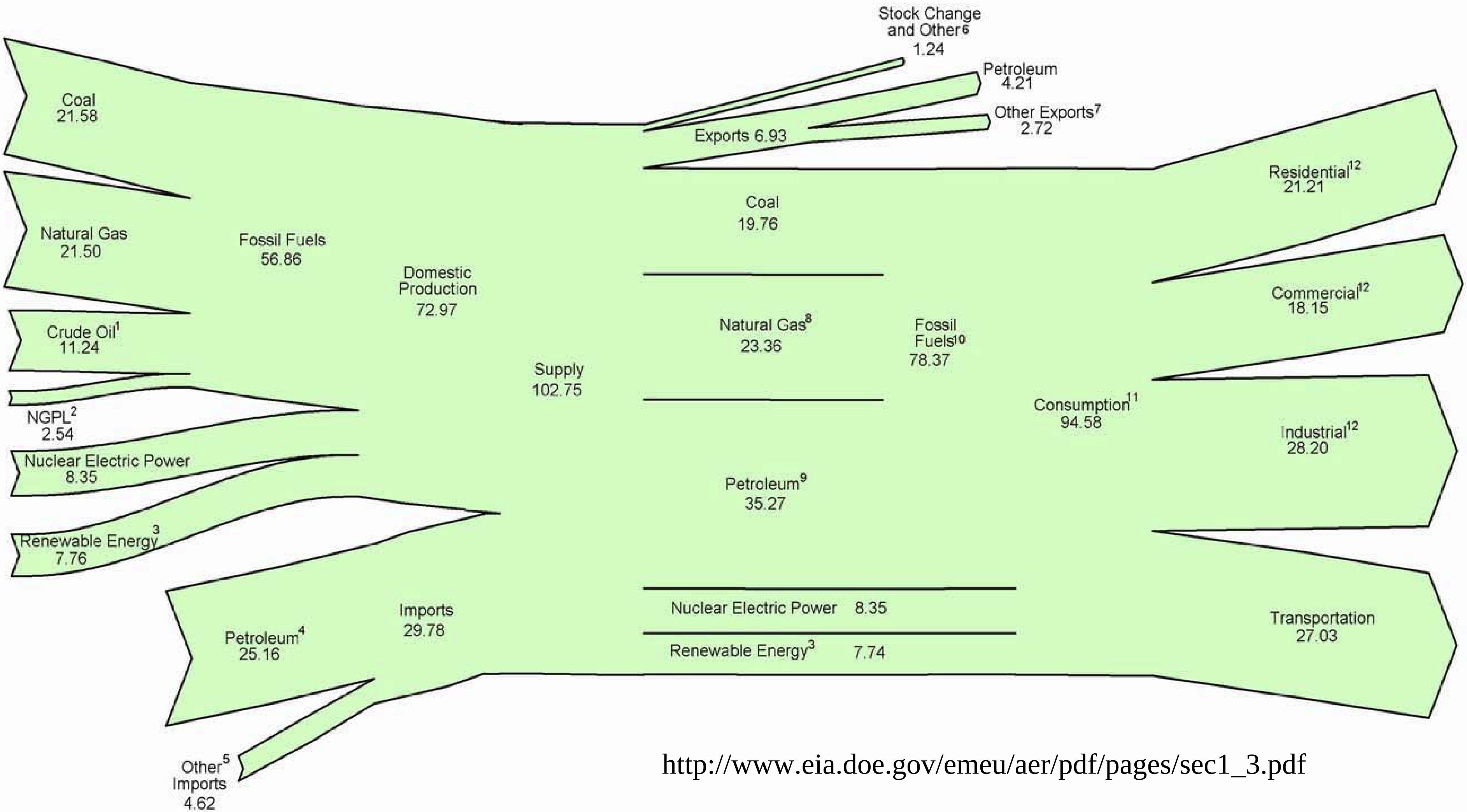
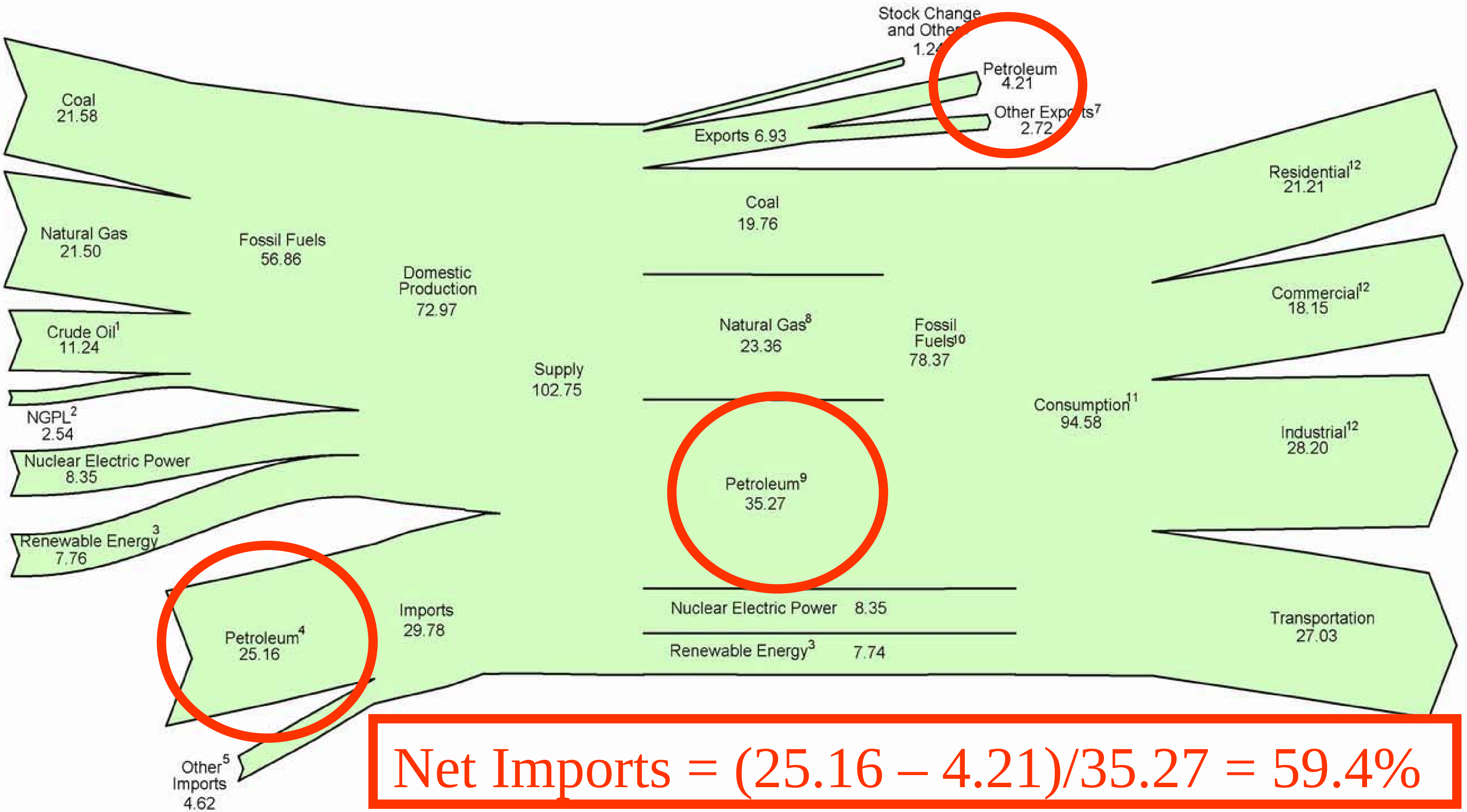
Energy Flow in the United States (2009)



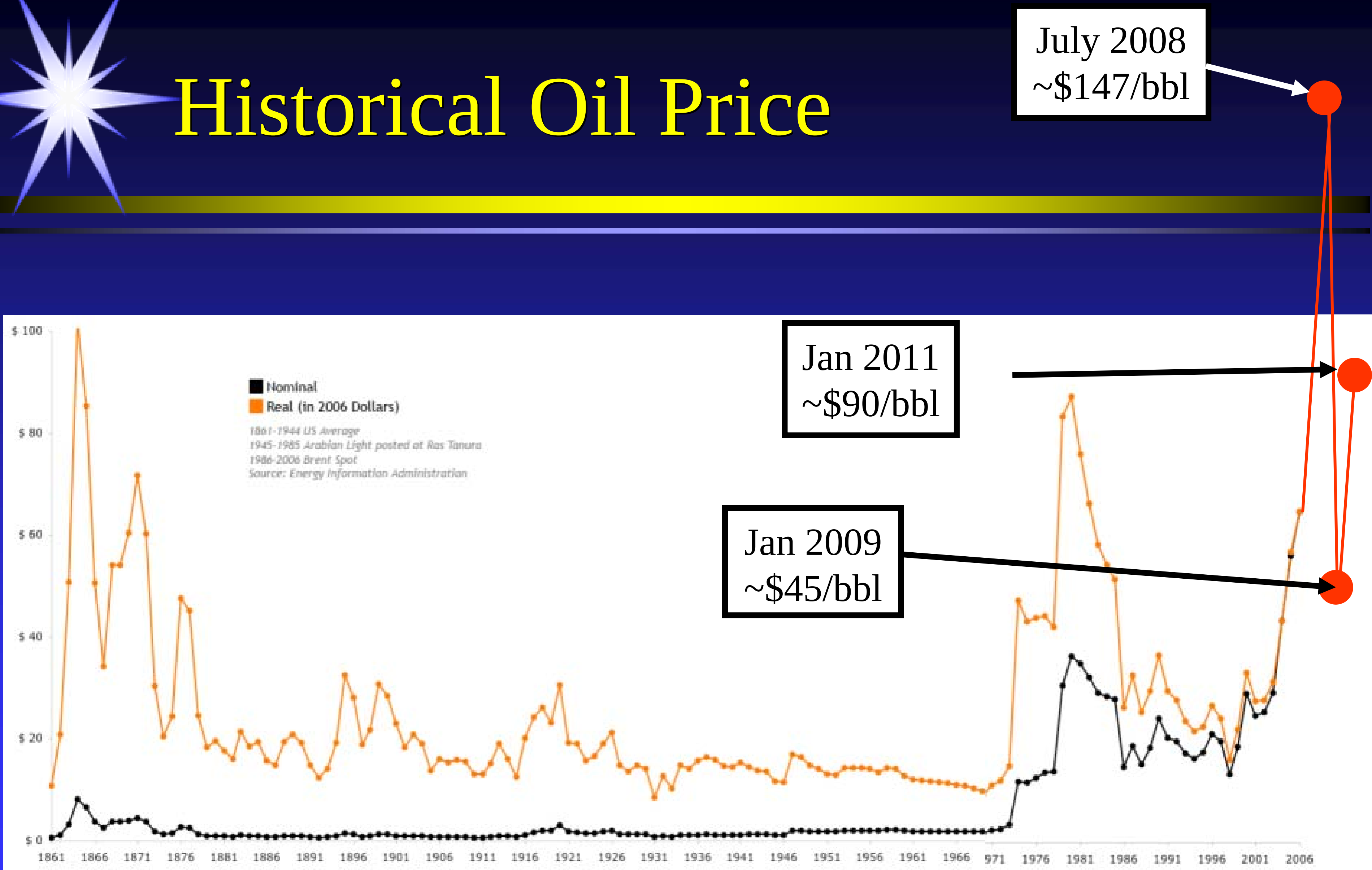
http://www.eia.doe.gov/emeu/aer/pdf/pages/sec1_3.pdf

Energy Flow in the United States (2009)



Net Imports = (25.16 – 4.21)/35.27 = 59.4%

Historical Oil Price



http://en.wikipedia.org/wiki/Oil_price_increases_of_2004-2006

U.S. Oil Trade Deficit (2009)

$$\frac{20.6\ \text{mill bbl consumption}}{\text{day}} \times \frac{0.59\ \text{bbl import}}{\text{bbl consumption}} \times \frac{\$90}{\text{bbl}} = \$1.1\ \text{billion/day}$$

U.S. Oil Trade Deficit (2009)

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$\boxed{\$400\text{ billion/yr}}$ Oil imports

U.S. Oil Trade Deficit (2009)

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$400 billion/yr — Oil imports

$379 billion/yr — Total imports

http://www.americaneconomicalert.org/ticker_home.asp

Driving Forces

- Growing population
- Rising standard of living
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- Global warming

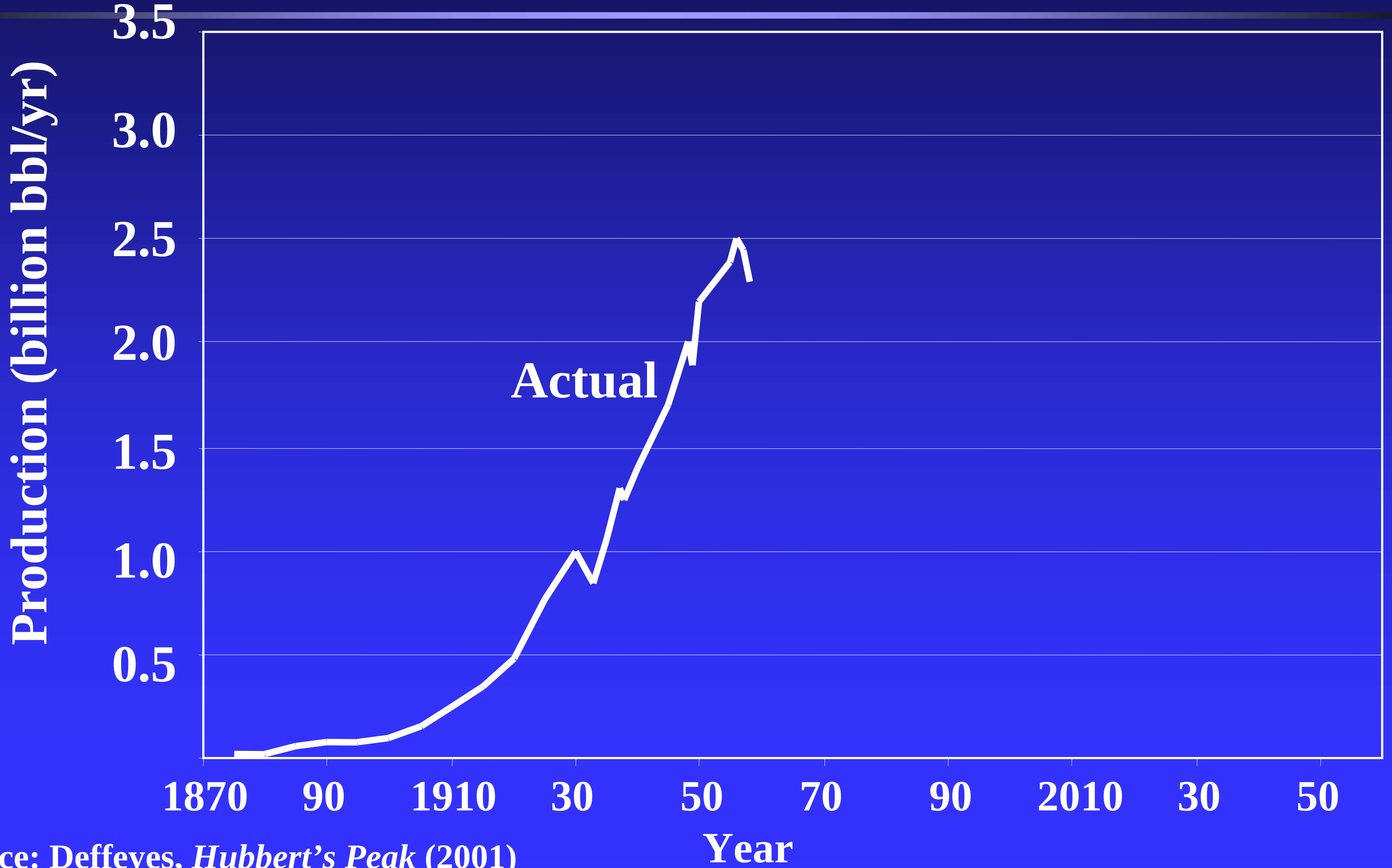
M. King Hubbert (1903-89)

American geophysicist

Shell Oil research laboratory

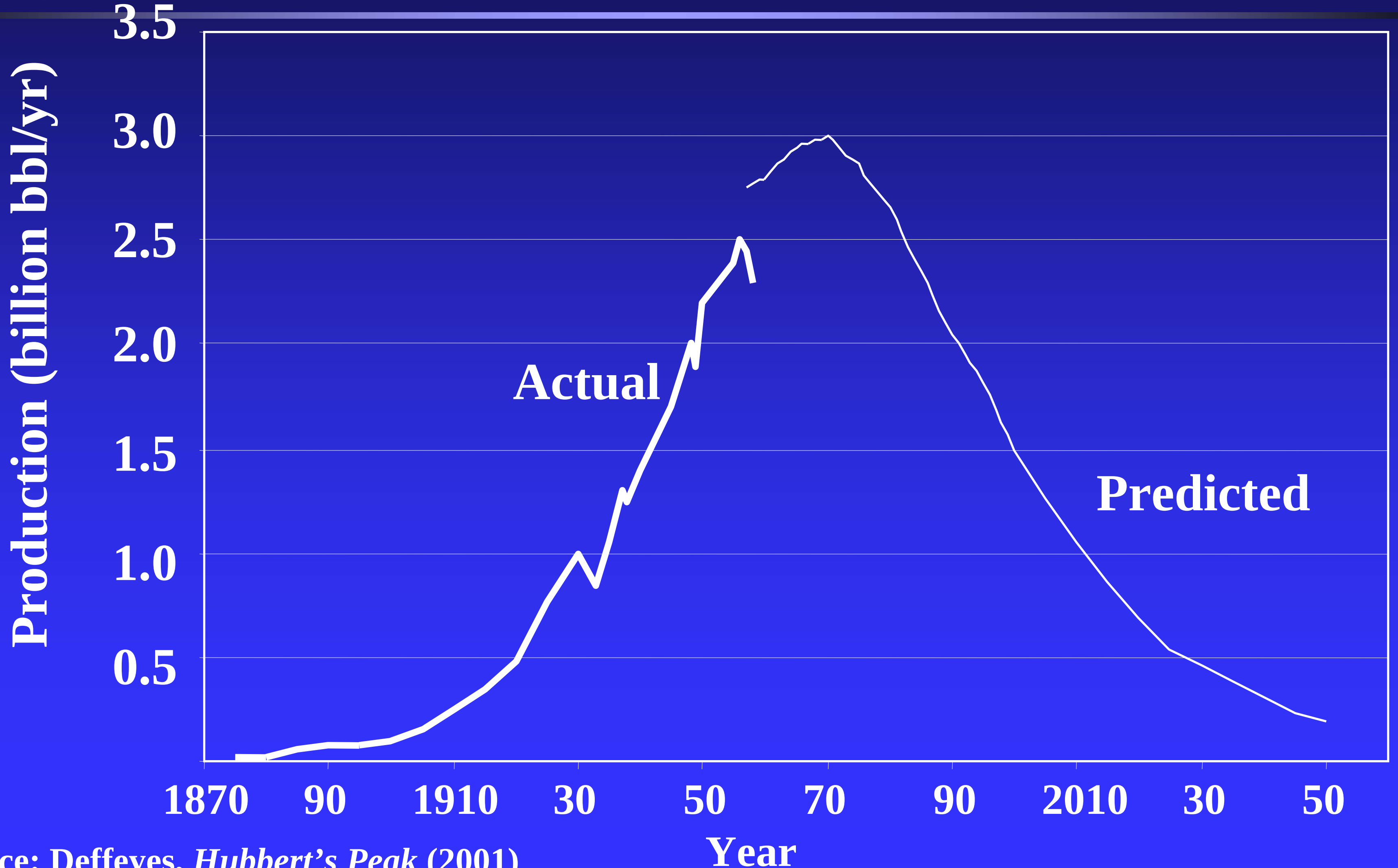
Houston, TX

US Oil Production Data through 1956



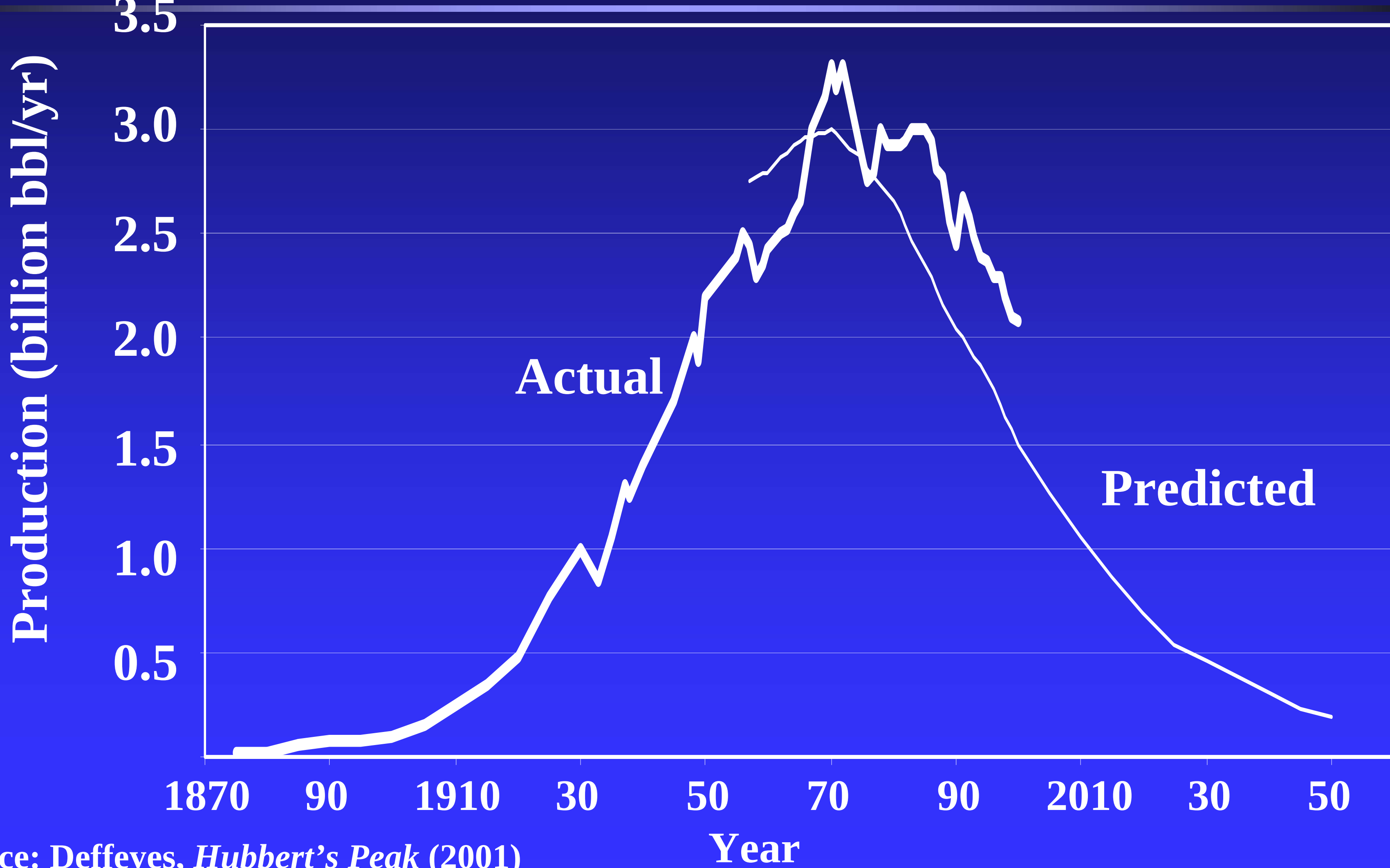
Source: Deffeyes, *Hubbert's Peak* (2001)

US Oil Production
Hubbert's Prediction (1956)



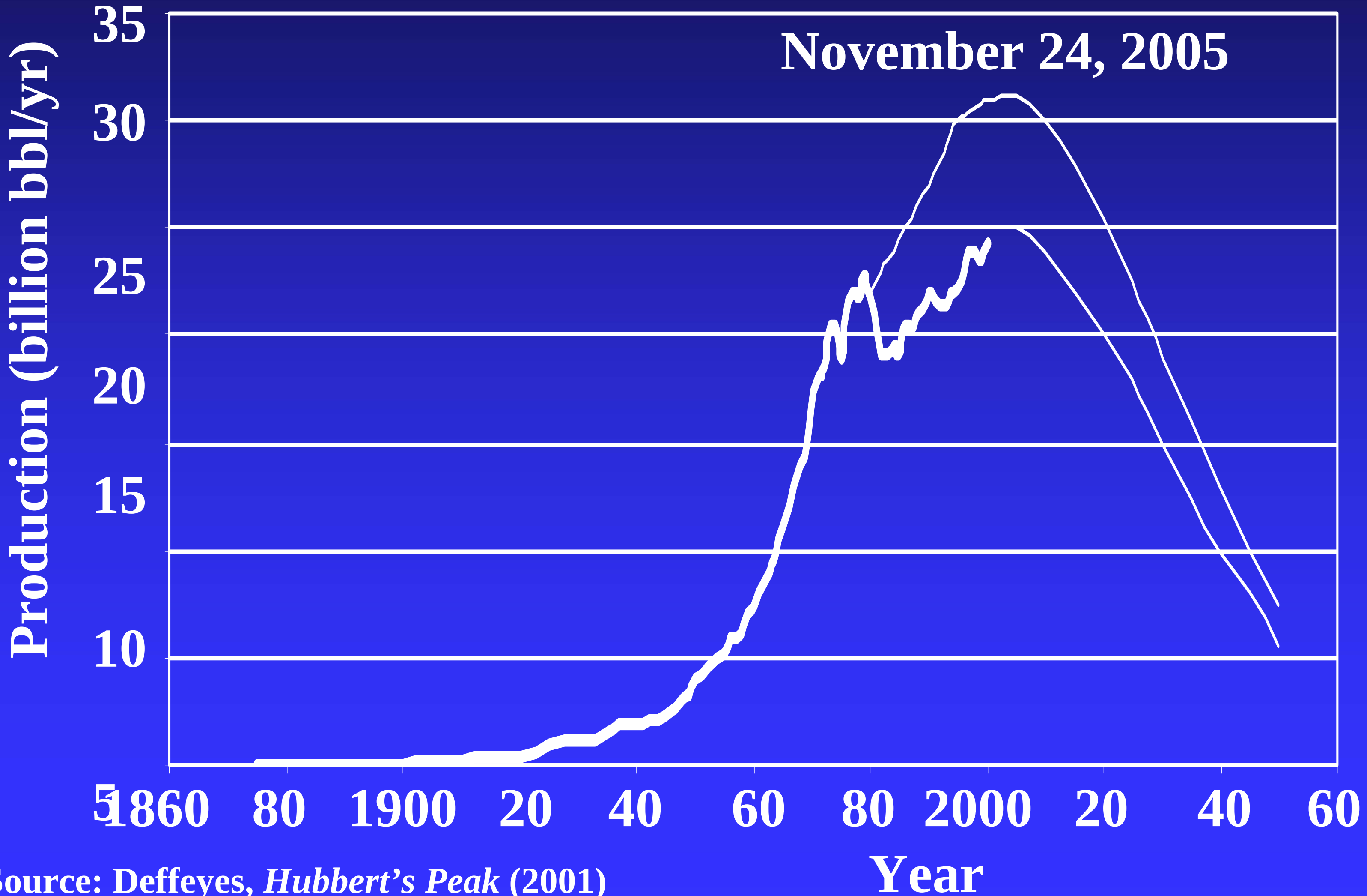
Source: Deffeyes, *Hubbert's Peak* (2001)

US Oil Production
How well did he do?



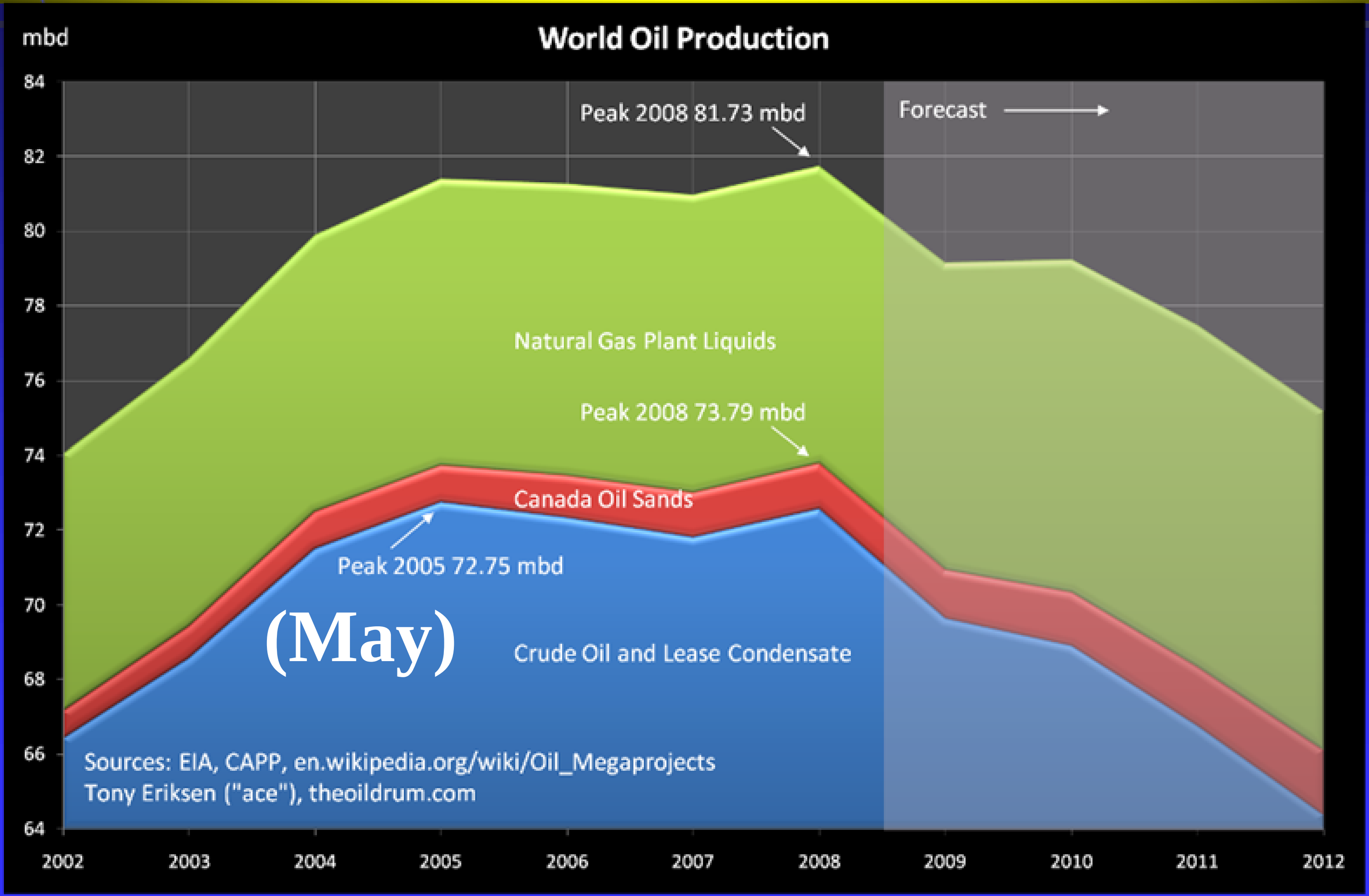
Source: Deffeyes, *Hubbert's Peak* (2001)

World Oil Production
Deffeyes Prediction (2001)



Source: Deffeyes, *Hubbert's Peak* (2001)

How good was his prediction?



http://www.hubbertpeak.com/

Driving Forces

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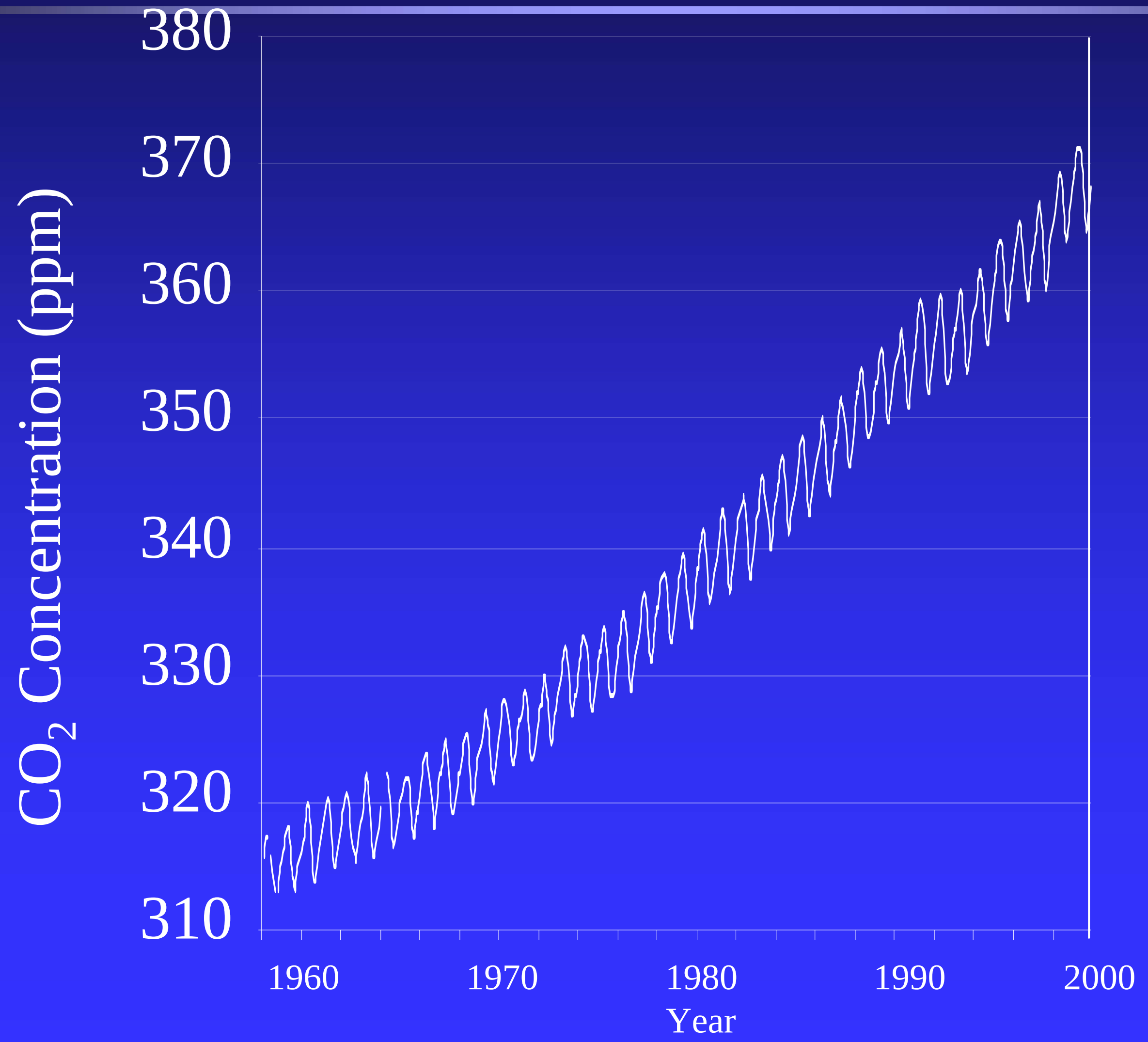
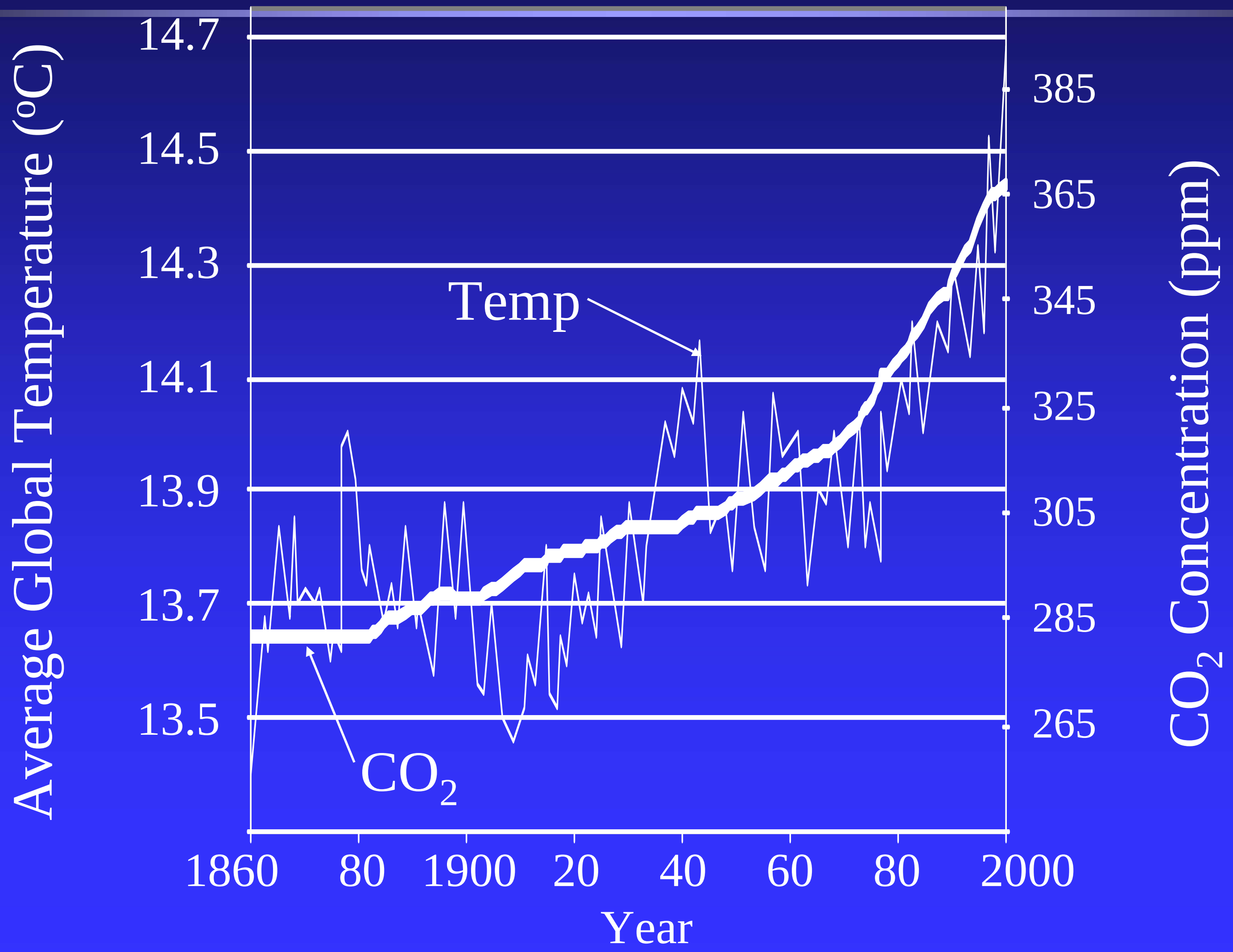
Recent CO_2 Concentration

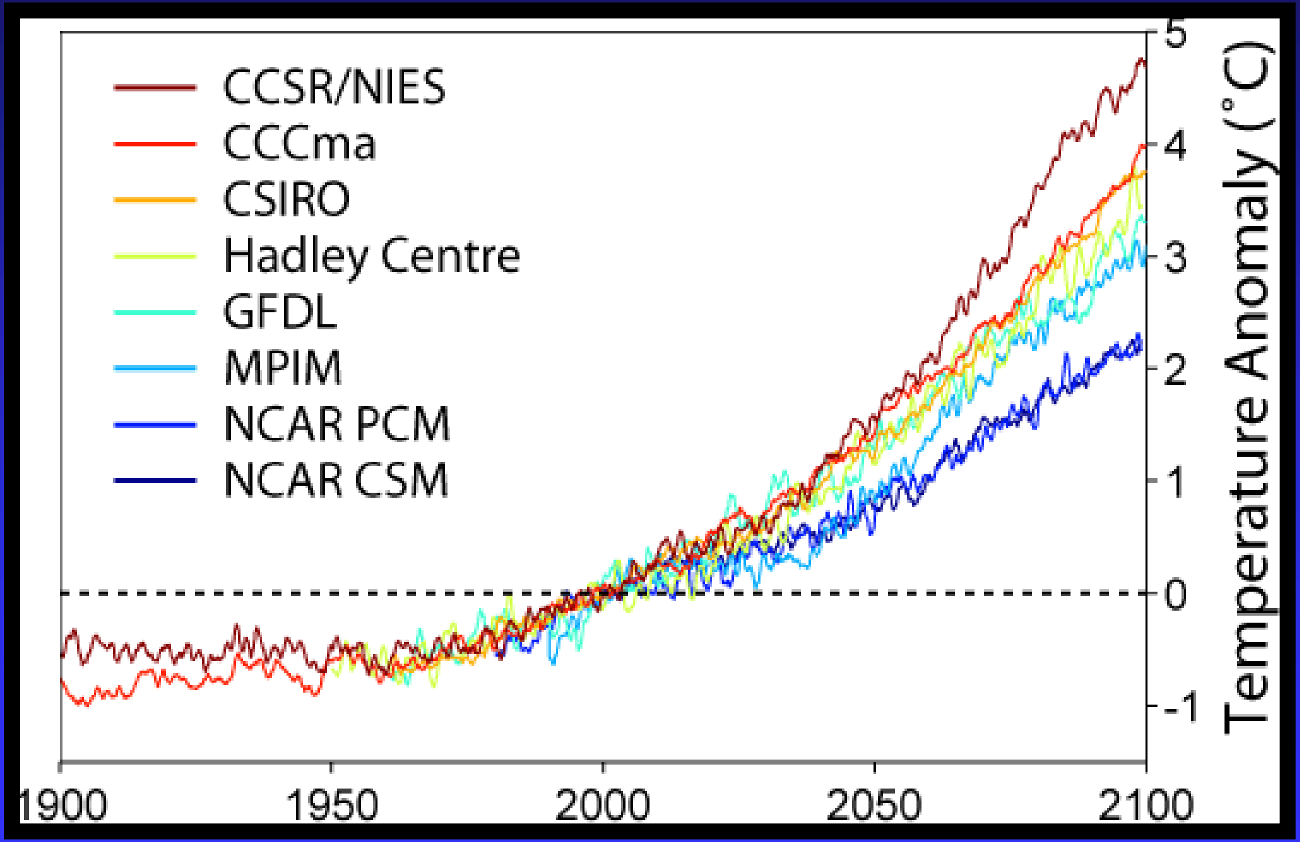


Mauna Loa Observatory

Recent Correlation



Global Warming Projections



Intergovernmental Panel on Climate Change
Business-as-usual scenario

How much Energy does an Average American Consume?

Primary Energy = 11.2 kW heat

How much Energy does an Average American Consume?

Primary Energy = 11.2 kW heat



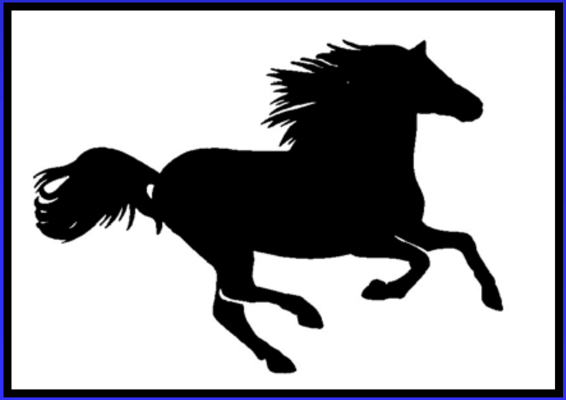
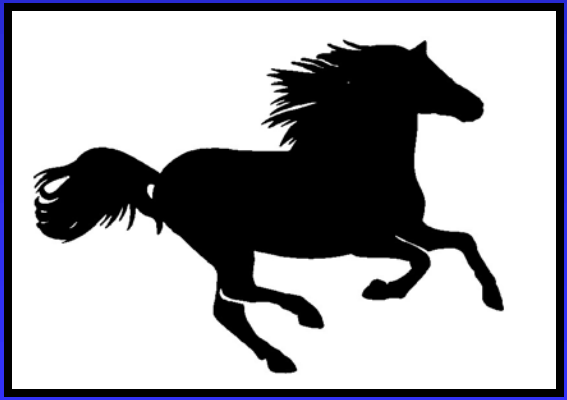
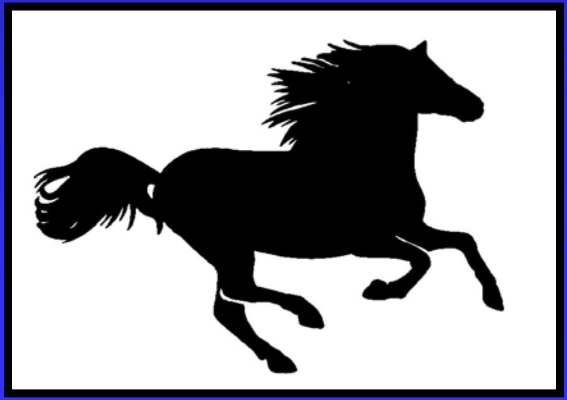



How much Energy does an Average American Consume?

Work = 2.24 kW

How much Energy does an Average American Consume?

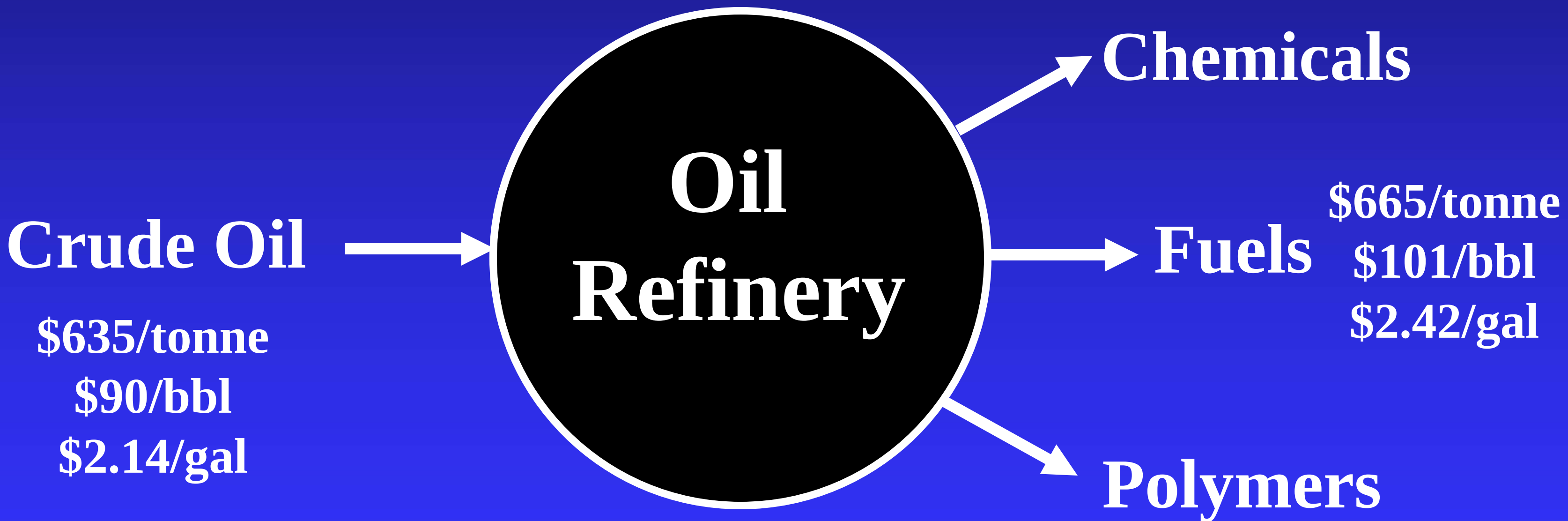
Work = 2.24 kW

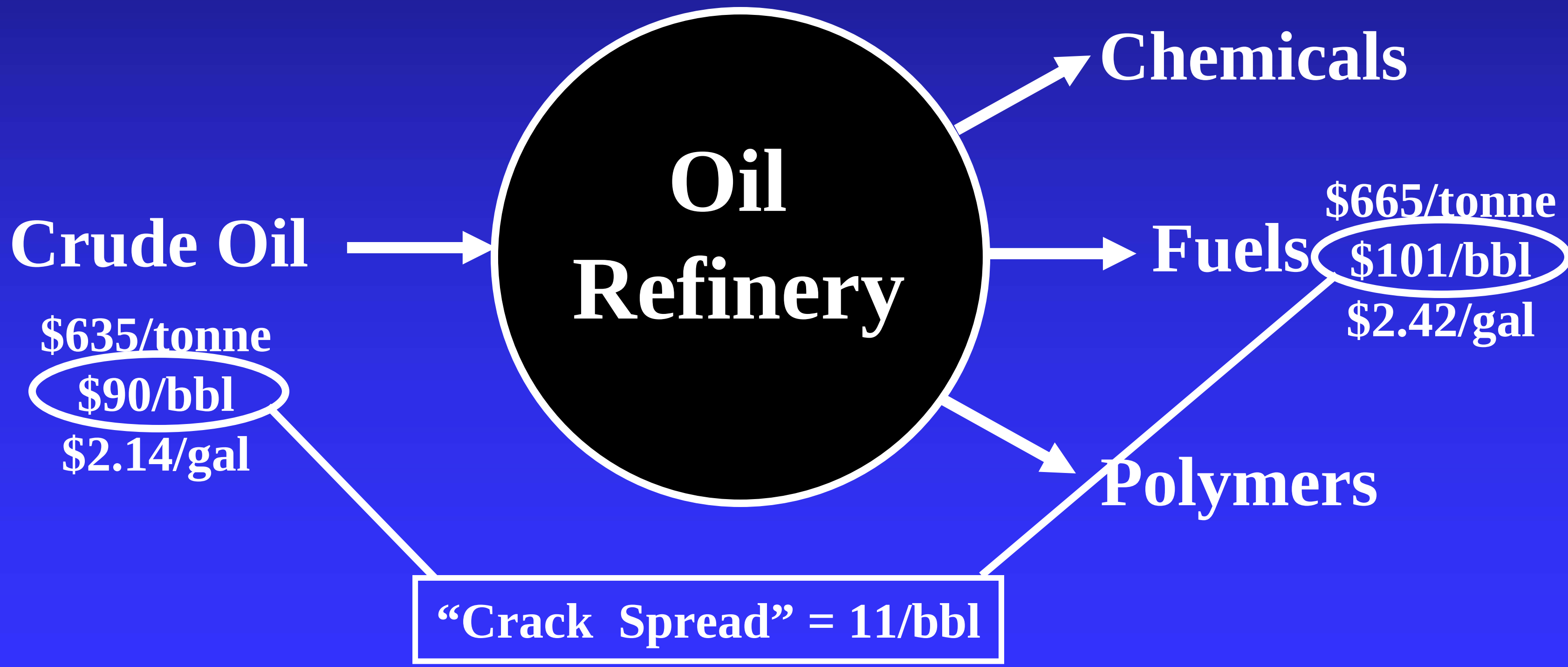
Outline

- Background
- Biofuels
- Advanced Engines

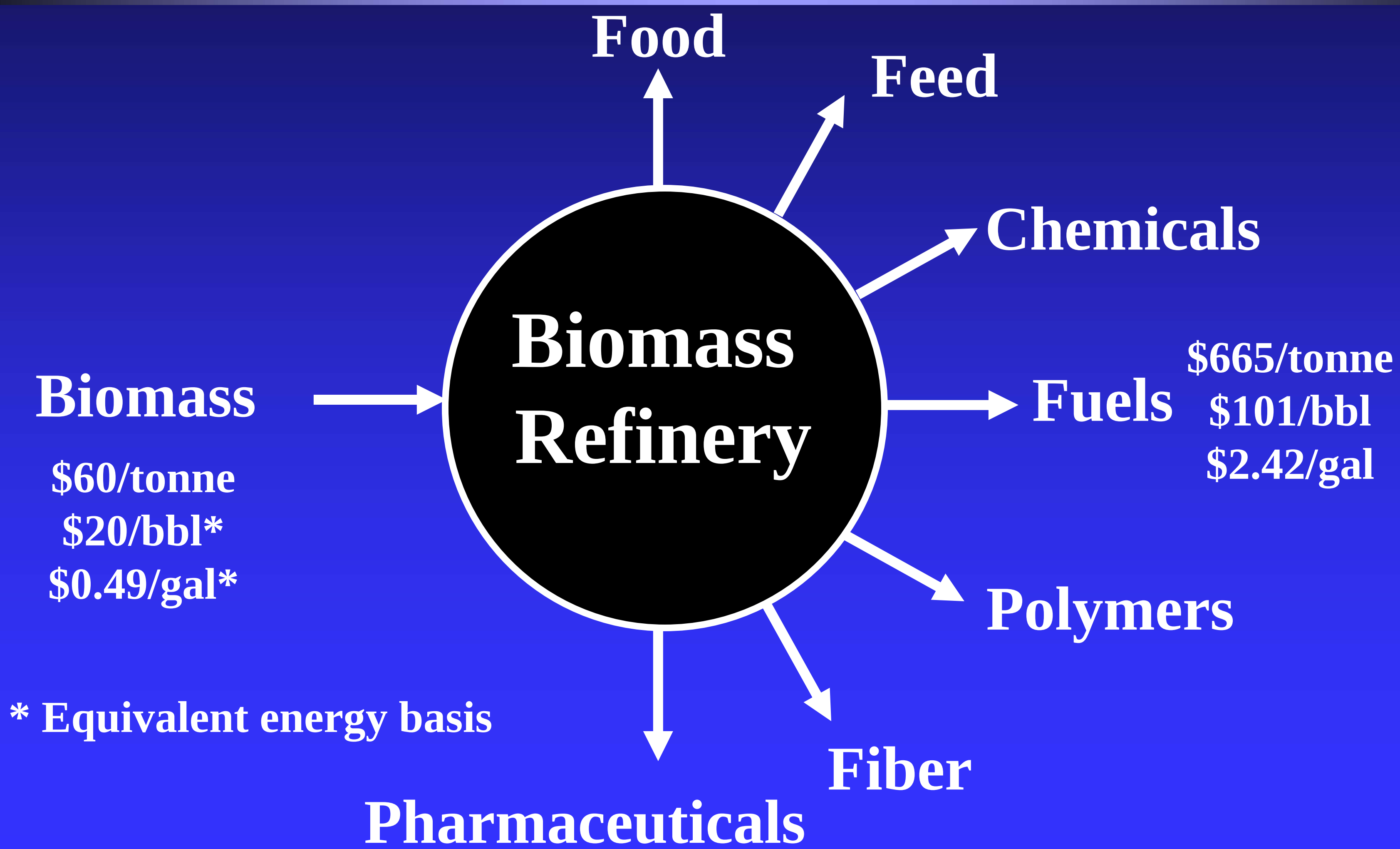
Oil Refinery



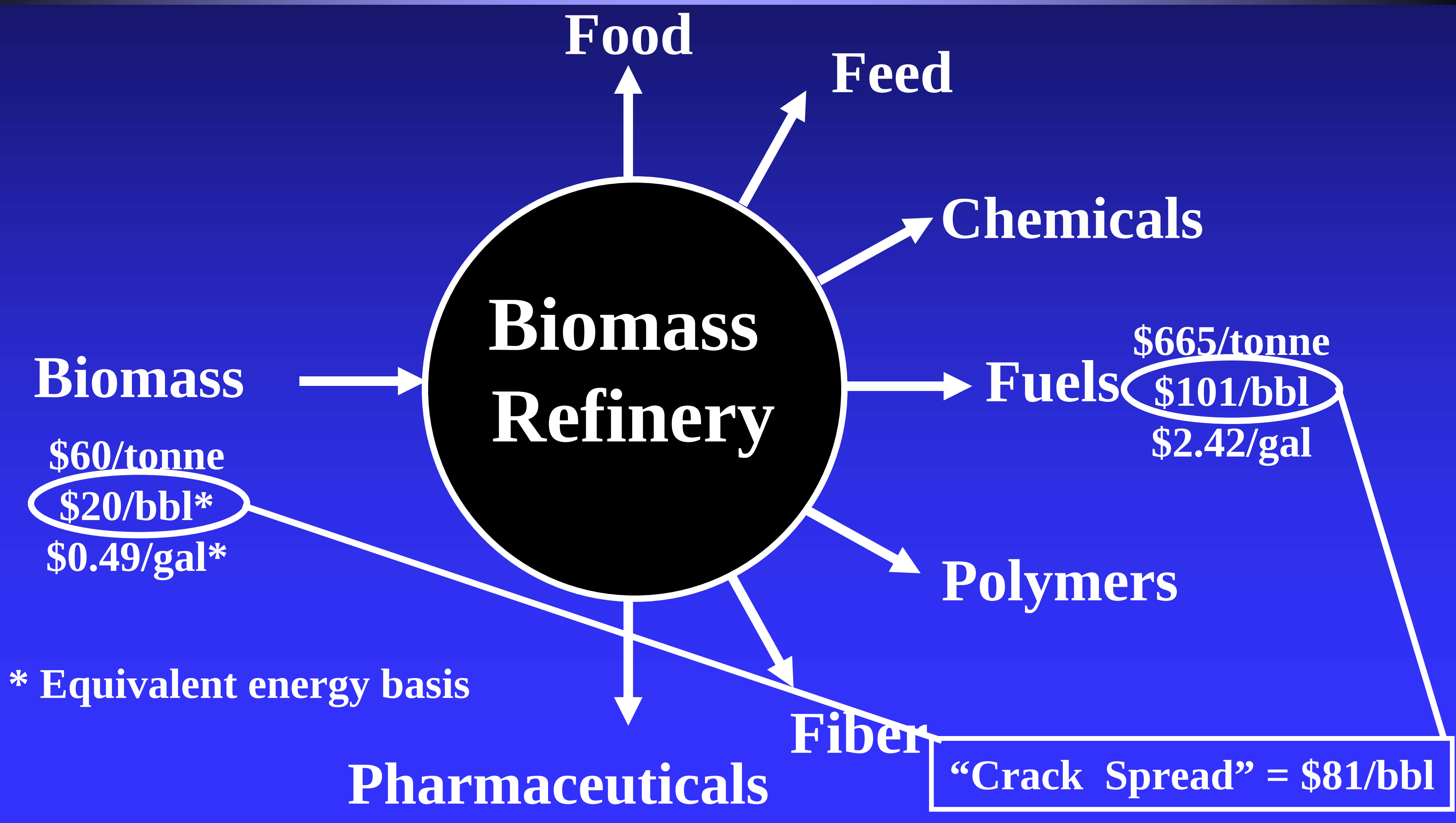
Oil Refinery



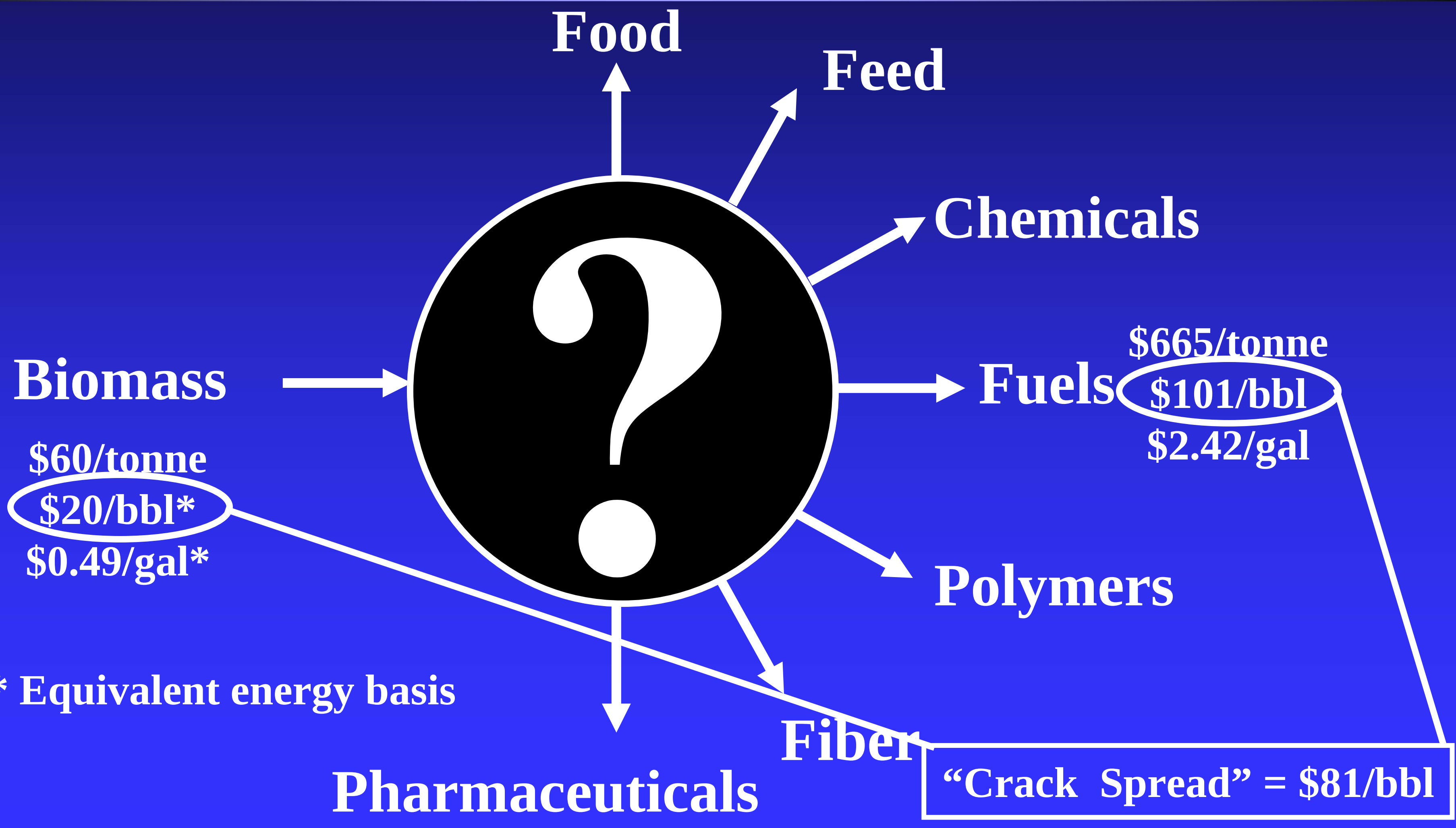
Biomass Refinery



Biomass Refinery



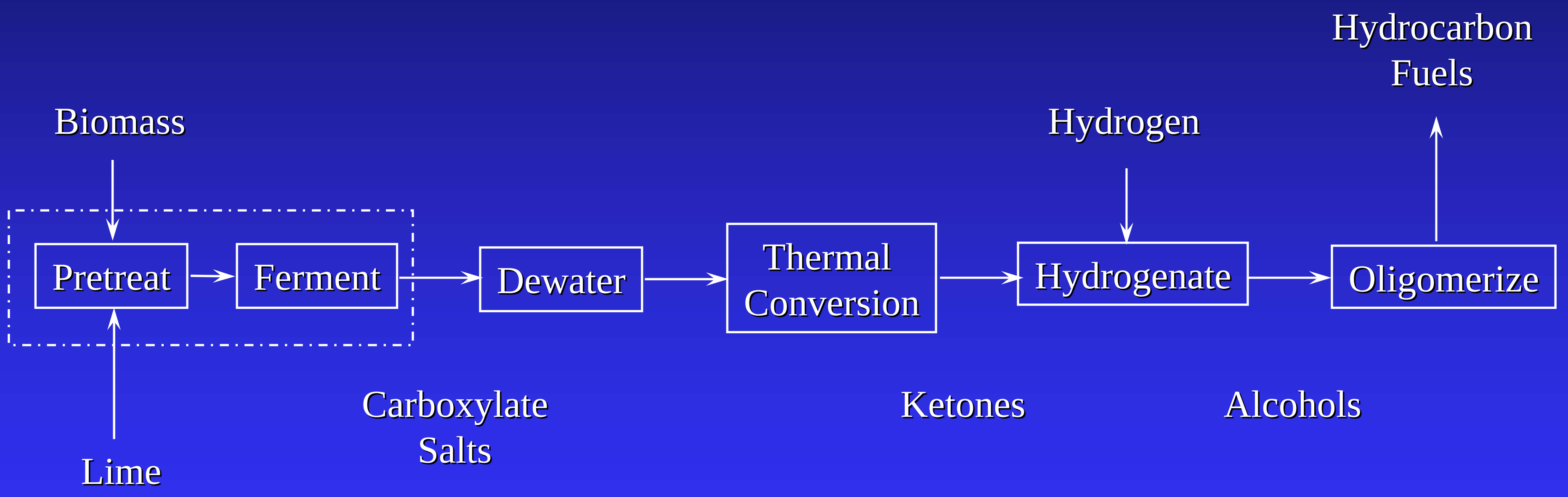
Biomass Refinery



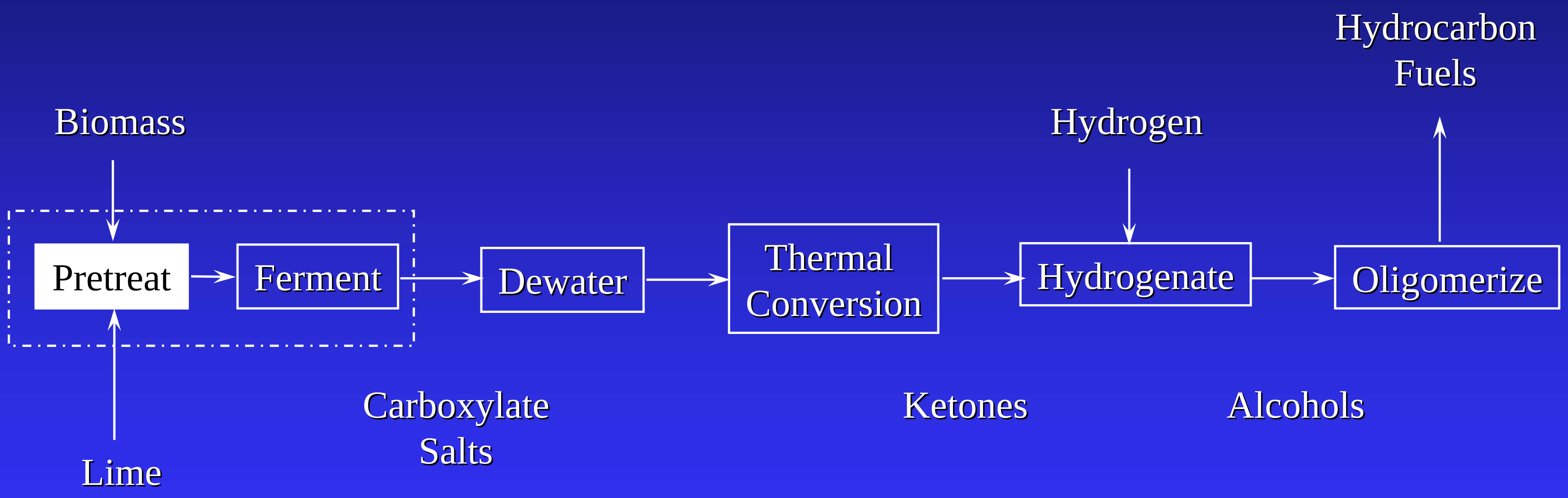
* Equivalent energy basis

MixAlco Process

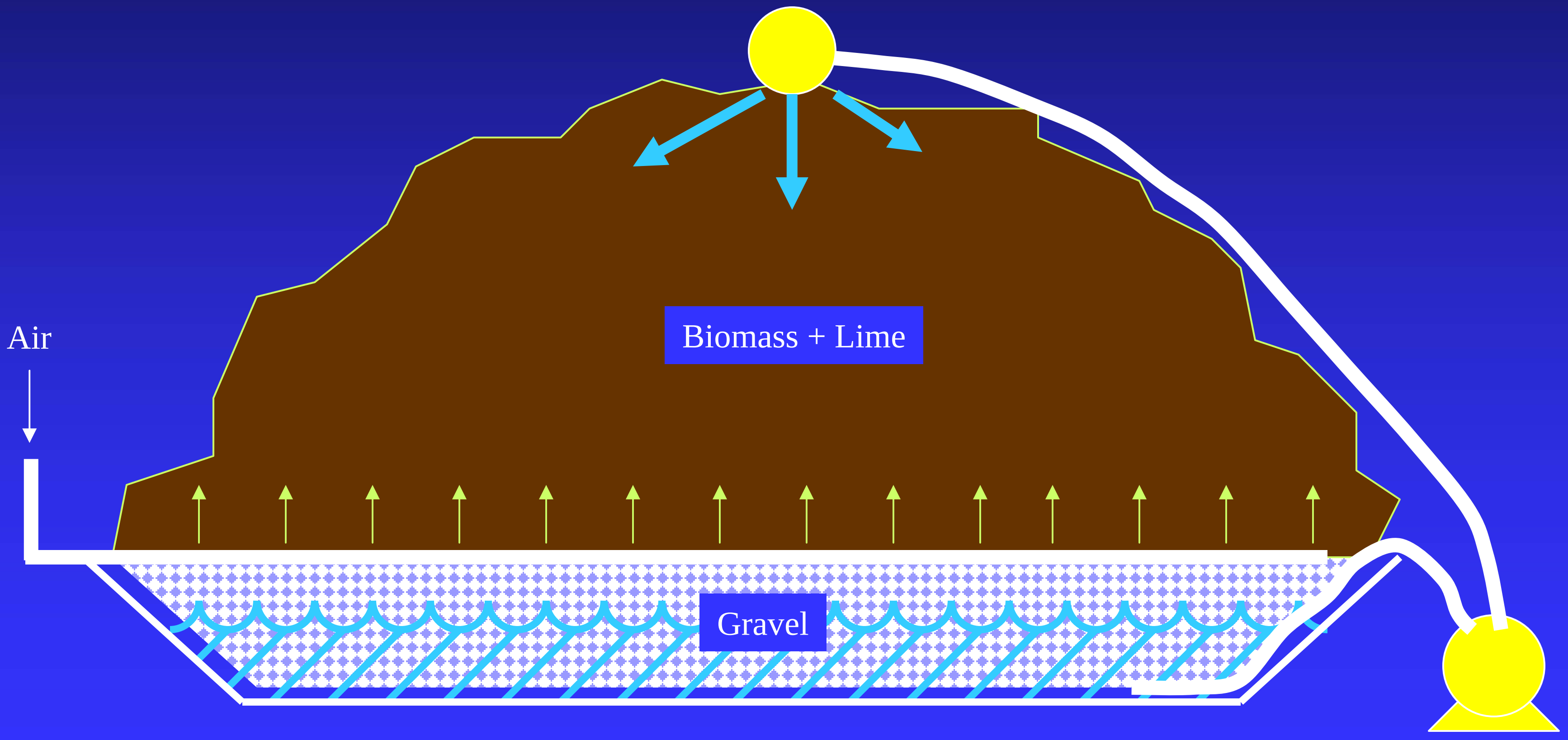
MixAlco Process



MixAlco Process



Advanced Lime Treatment

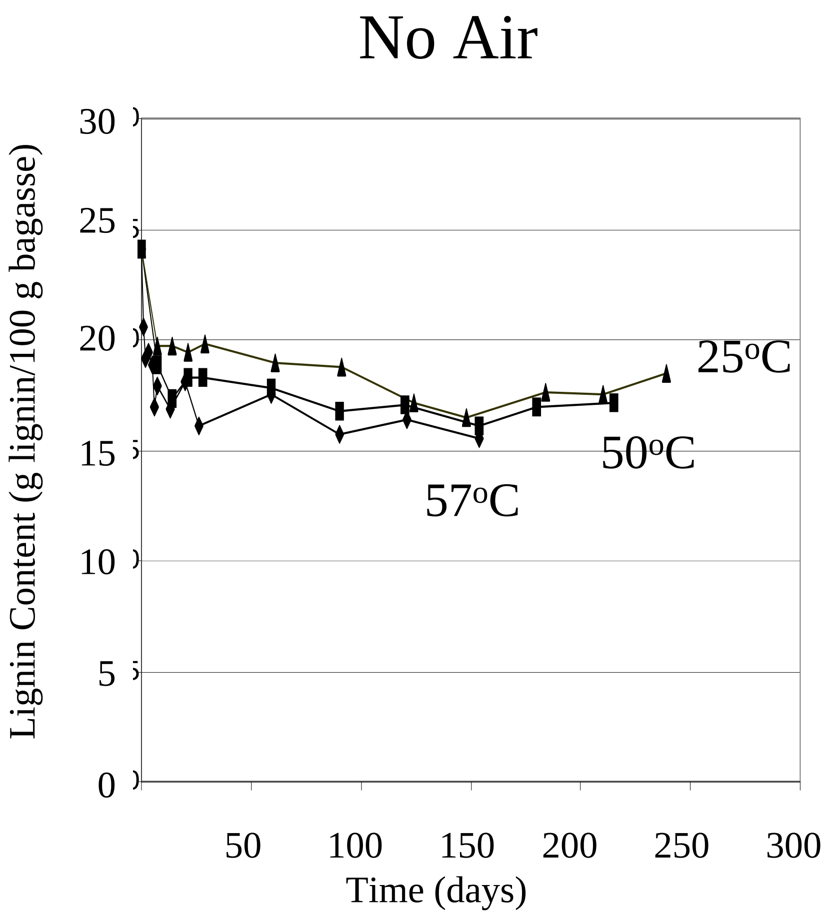


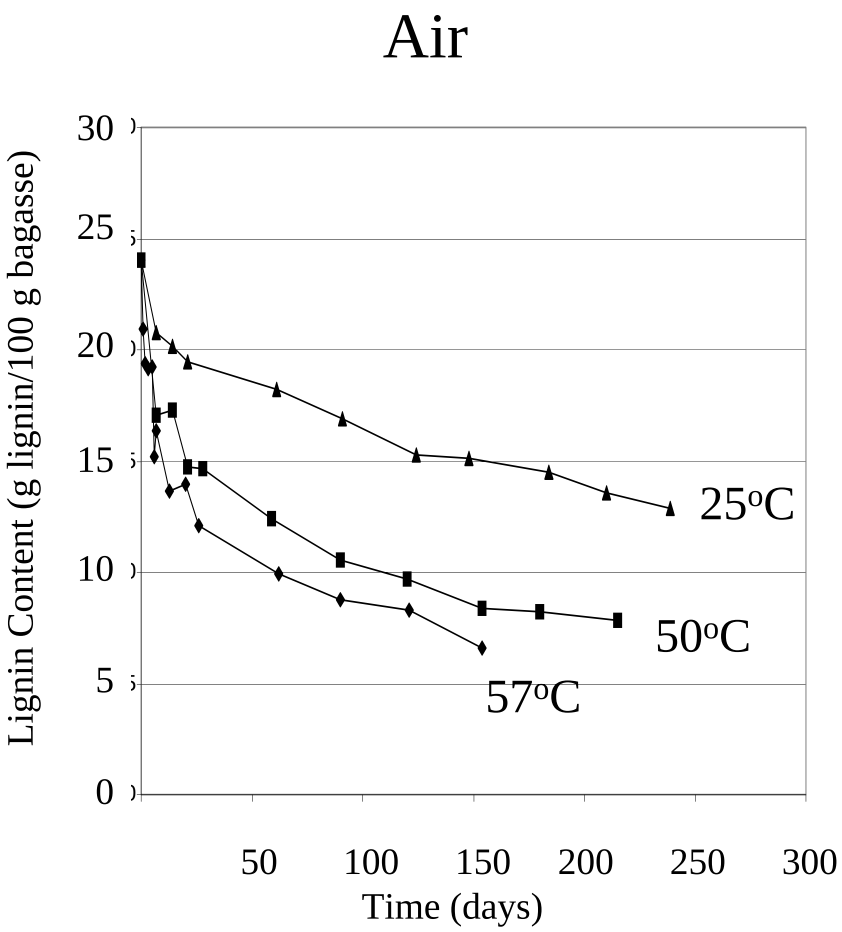
Building the Pile

~100 ft

Building the Pile

Lignin Removal





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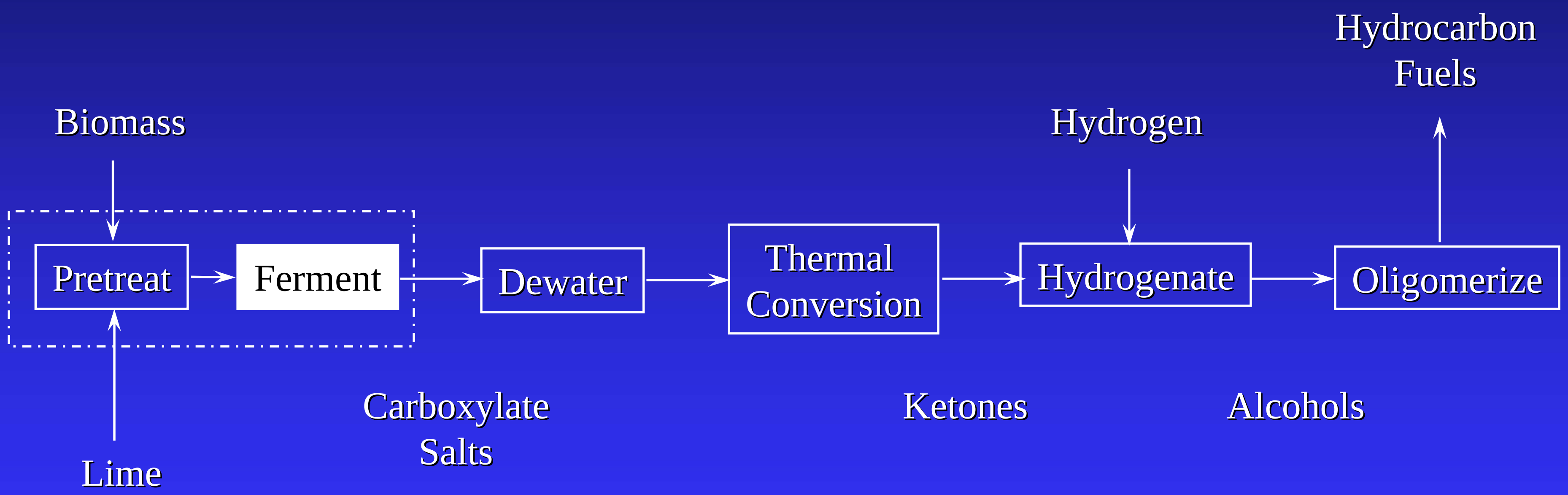

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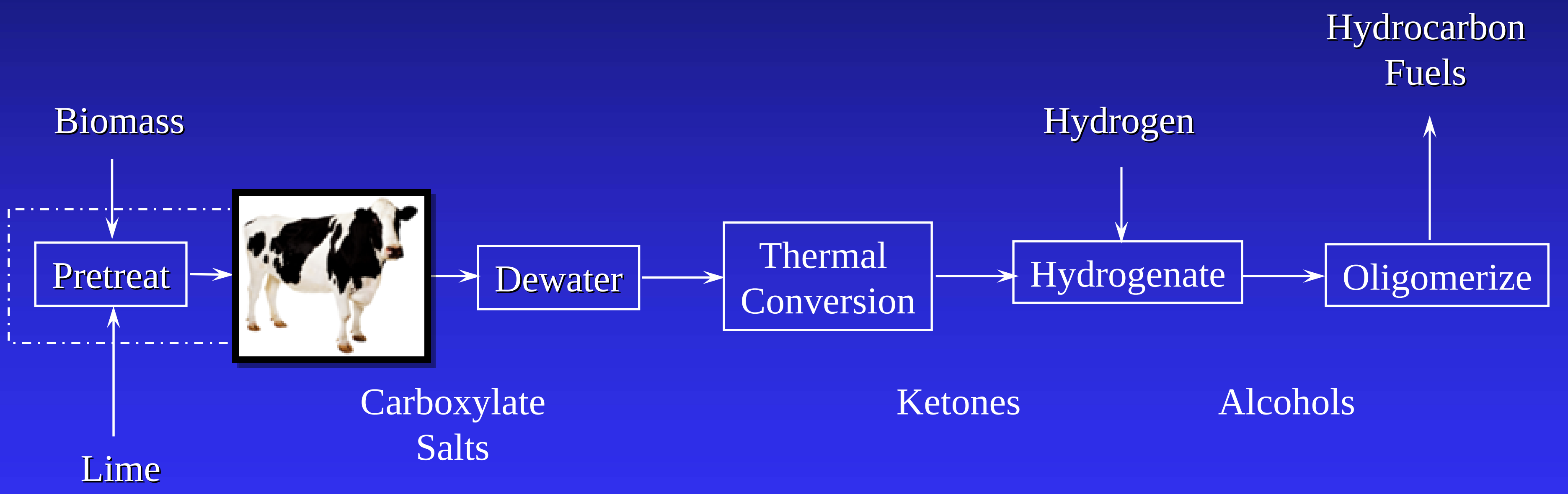

Environments where organic acids naturally form

- 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 + H_2

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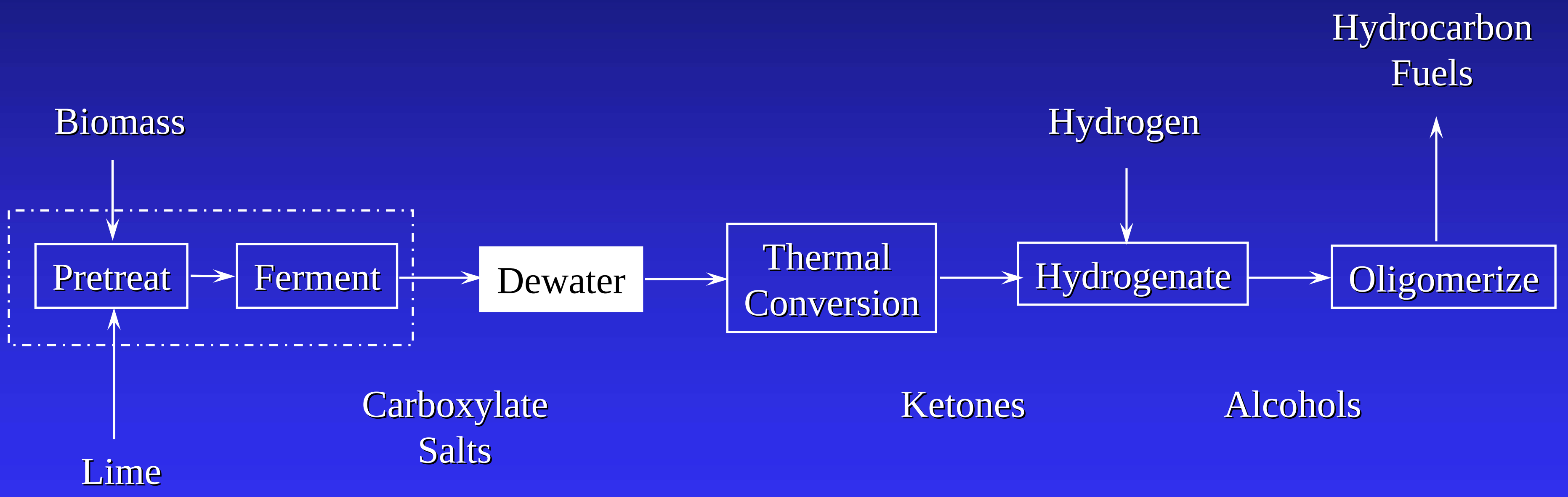
Methanogen inhibitor

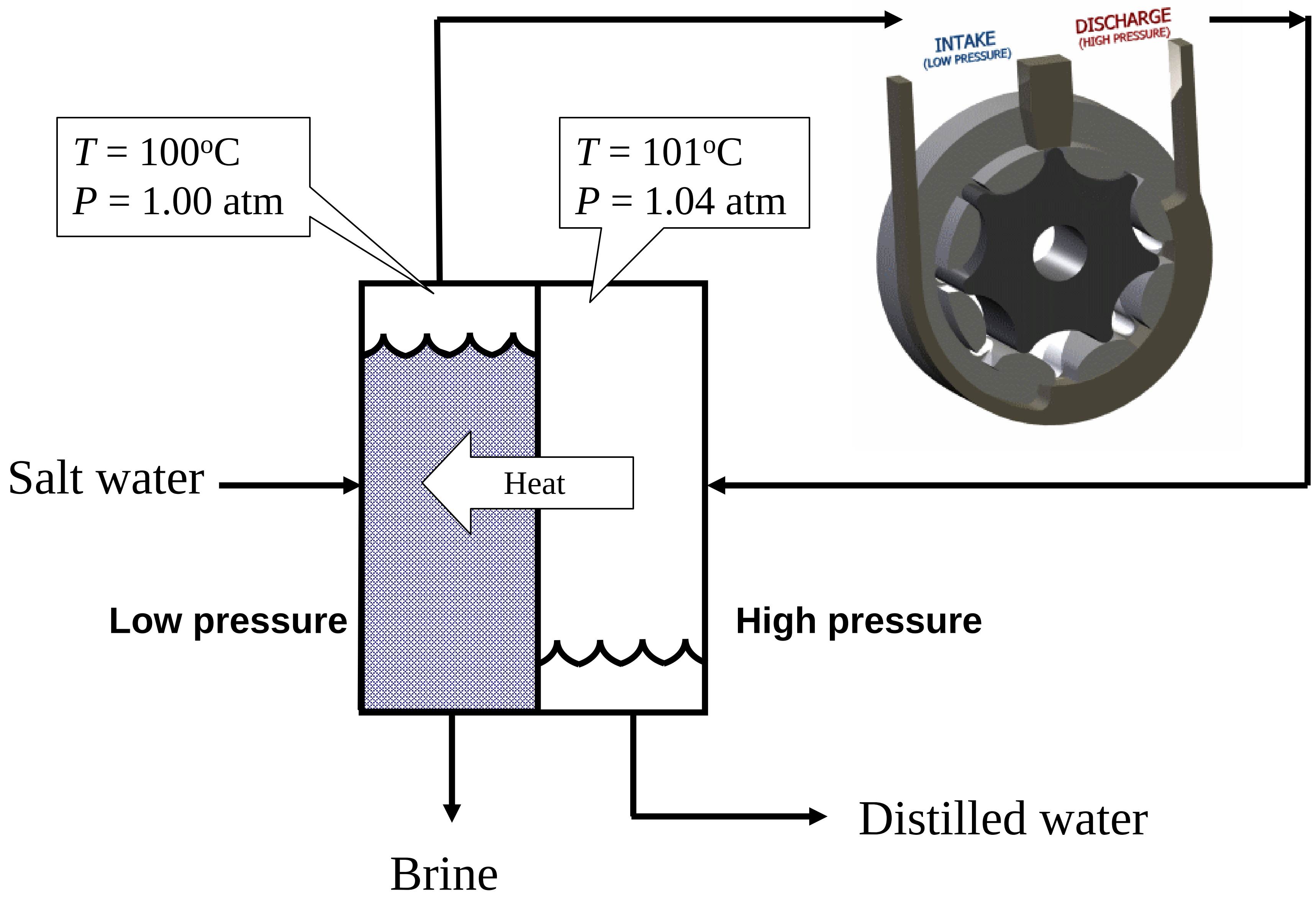
Typical Product Spectrum at Different Culture Temperatures

	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 %

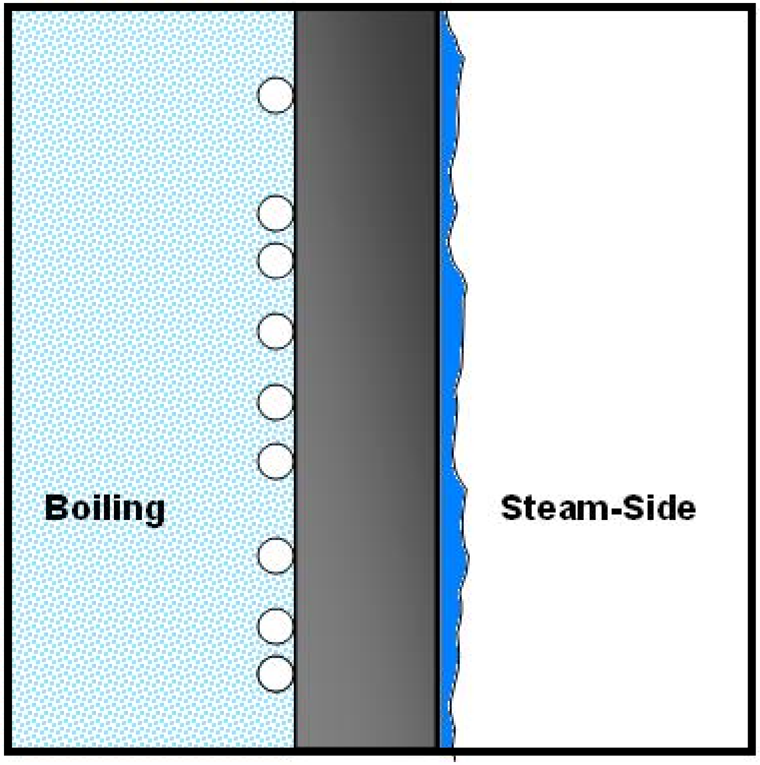
MixAlco Process



Vapor-Compression Desalination

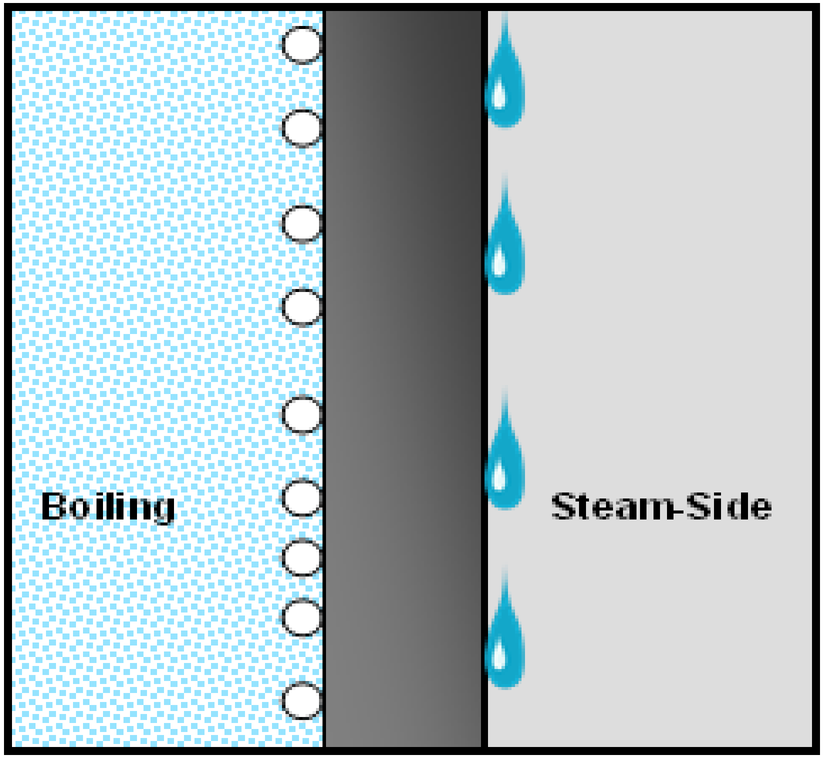


Filmwise Condensation



~2,000 Btu/(h·ft^2·^{o}F)

Dropwise Condensation

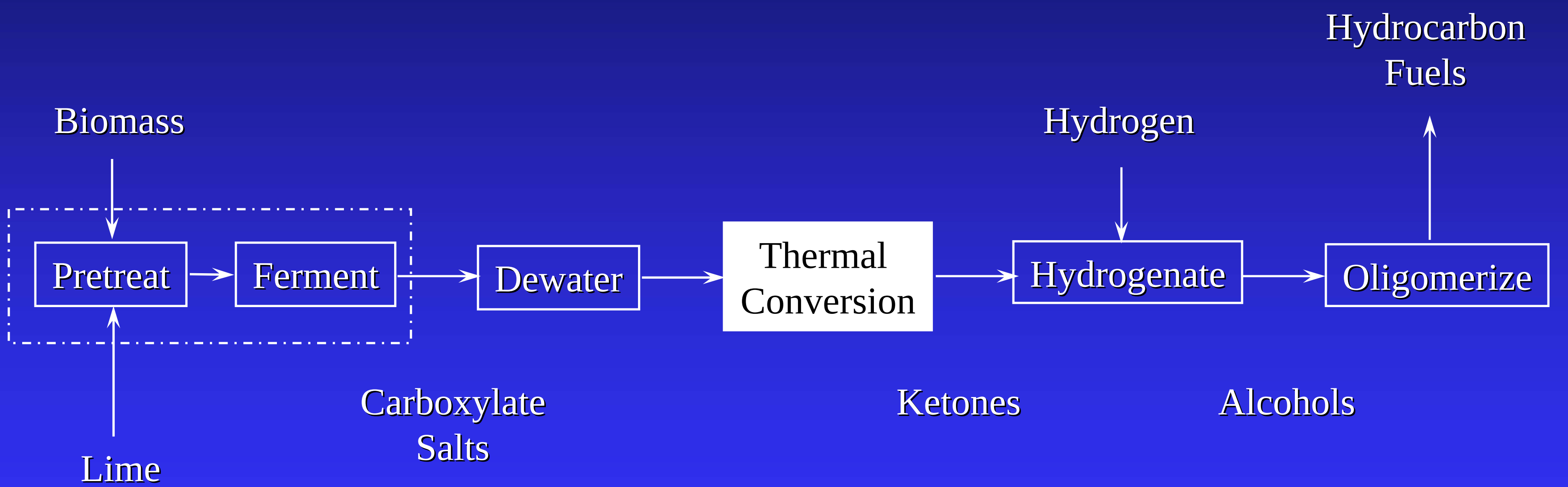


~42,000 Btu/(h·ft^2·^{o}F)

Laredo Desalination Project

Laredo Desalination Project

MixAlco Process



Thermal Conversion Stoichiometry

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

Calcium Acetate — Acetone

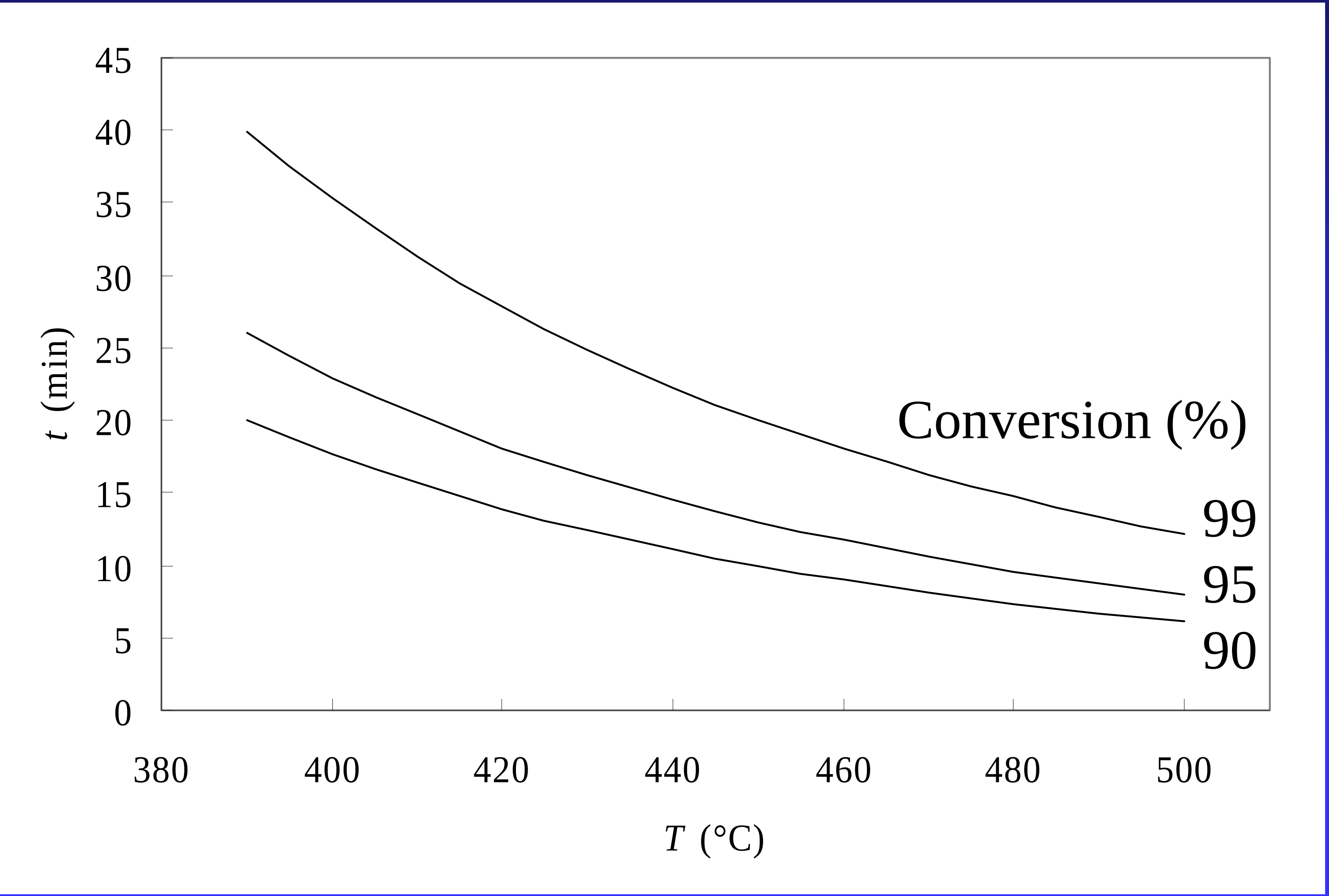
$$H_3CCH_2\overset{O}{\overset{\|}{C}}OCaO\overset{O}{\overset{\|}{C}}CH_2CH_3 \rightarrow H_3CCH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + CaCO_3$$

Calcium Propionate — Diethyl Ketone

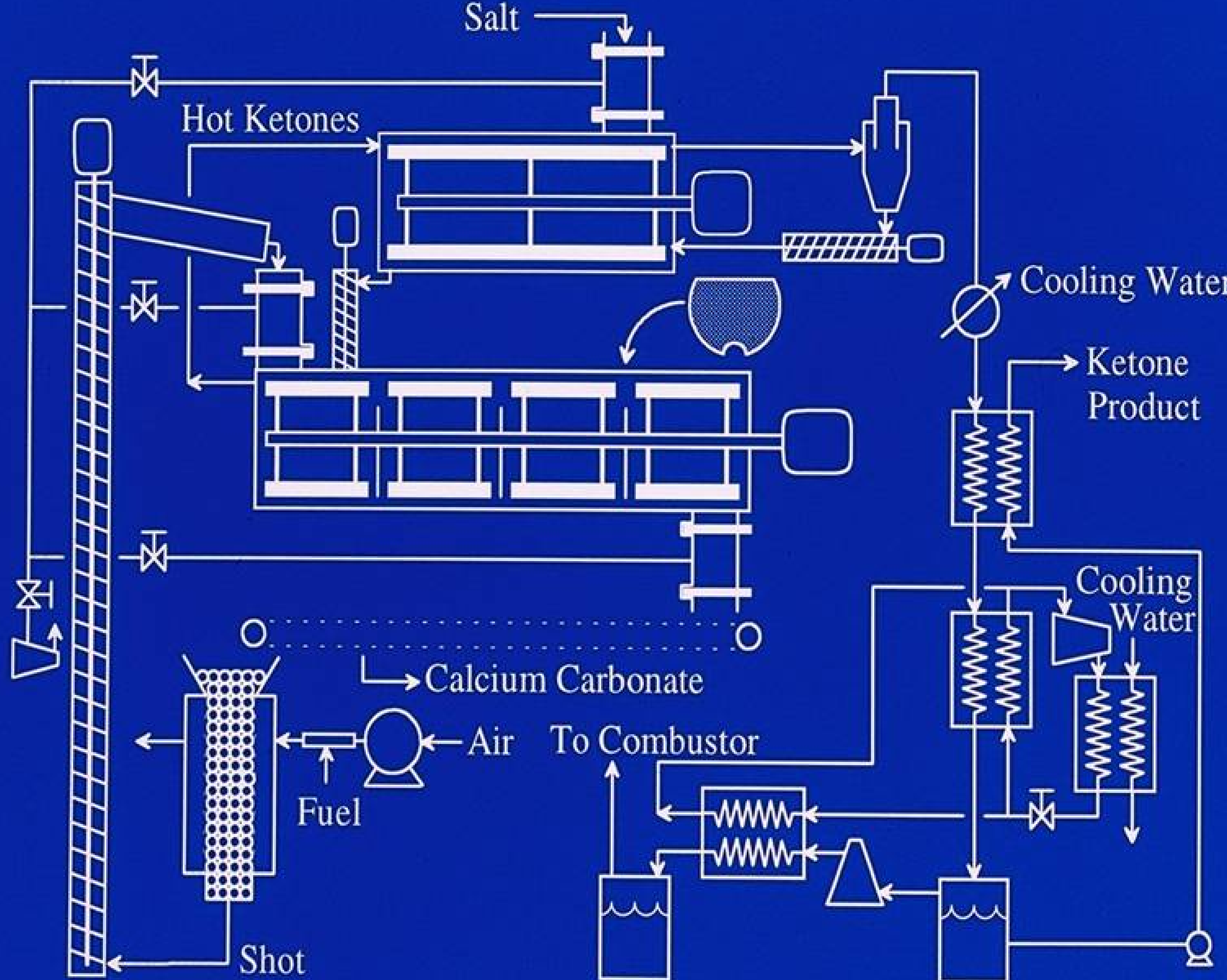
$$H_3CCH_2CH_2\overset{O}{\overset{\|}{C}}OCaO\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \rightarrow H_3CCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 + CaCO_3$$

Calcium Butyrate — Dipropyl Ketone

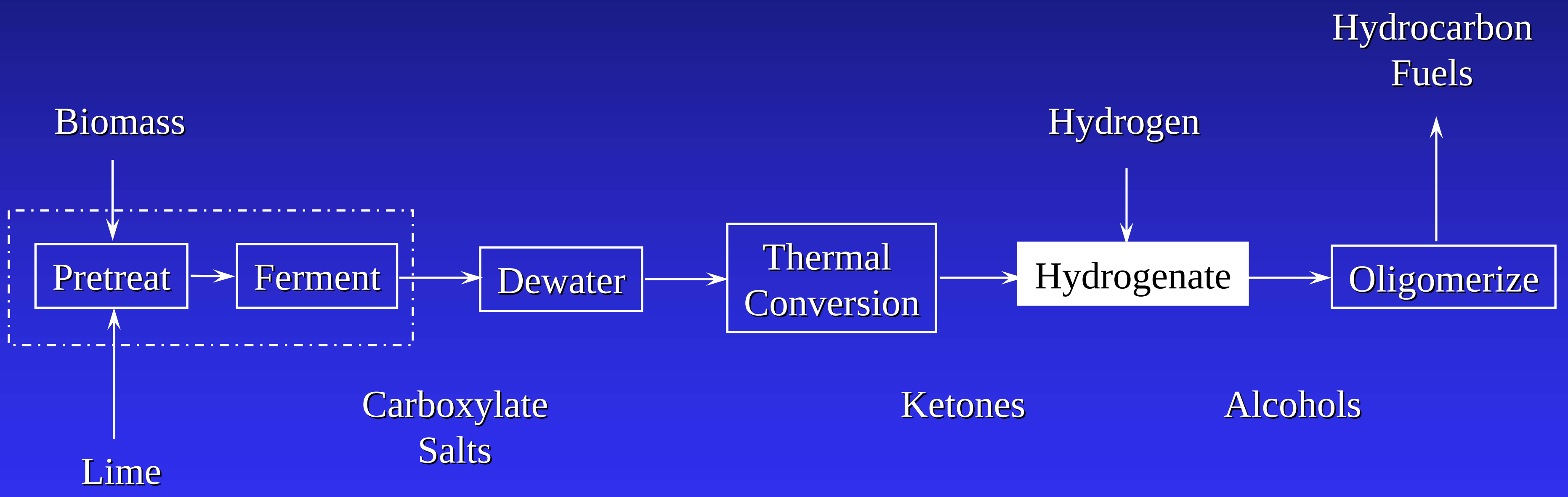
Thermal Conversion Kinetics



Thermal Conversion



MixAlco Process



Ketone Hydrogenation Stoichiometry

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

Acetone → Isopropanol

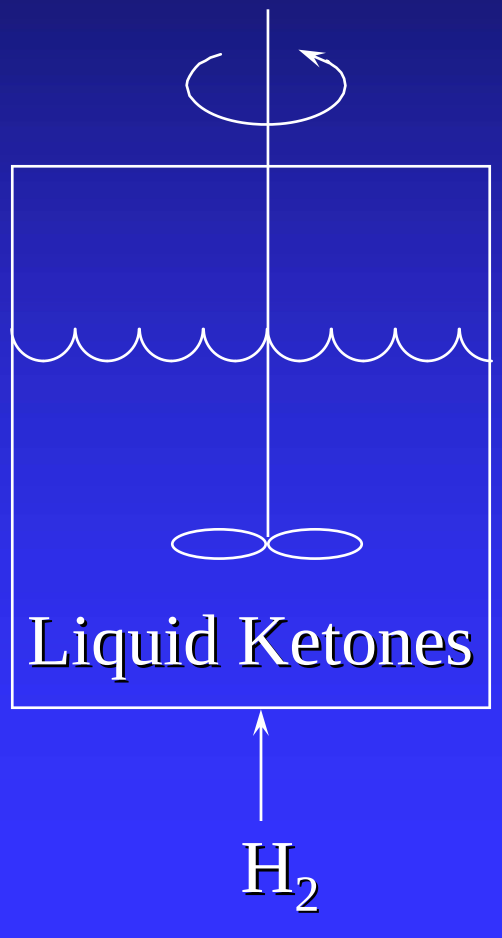
$$H_3C\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3 + H_2 \rightarrow H_3C\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}CH_2CH_3$$

Methyl Ethyl Ketone → 2-Butanol

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

Diethyl Ketone → 3-Pentanol

Ketone Hydrogenation

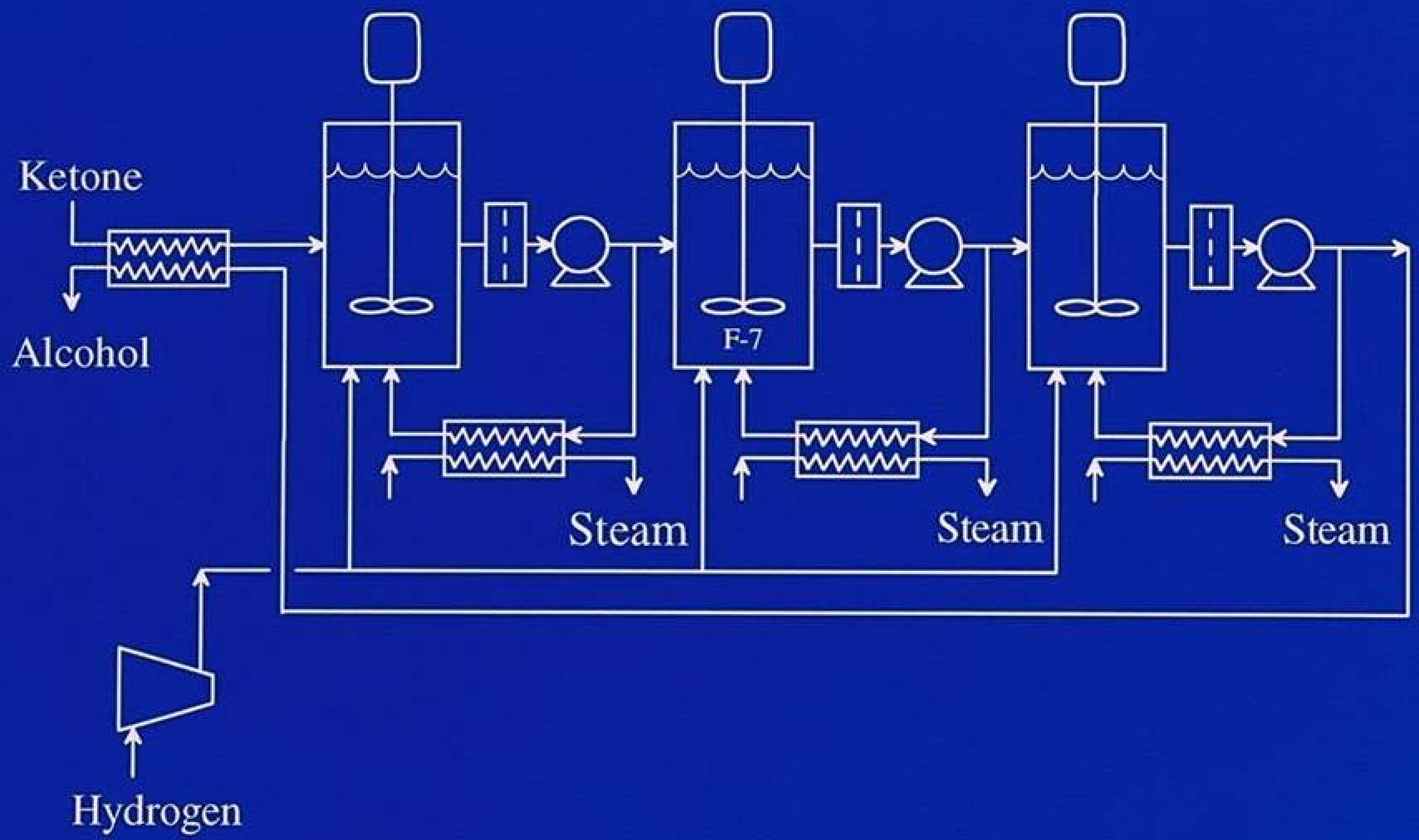


Catalyst = 200 g/L Raney nickel

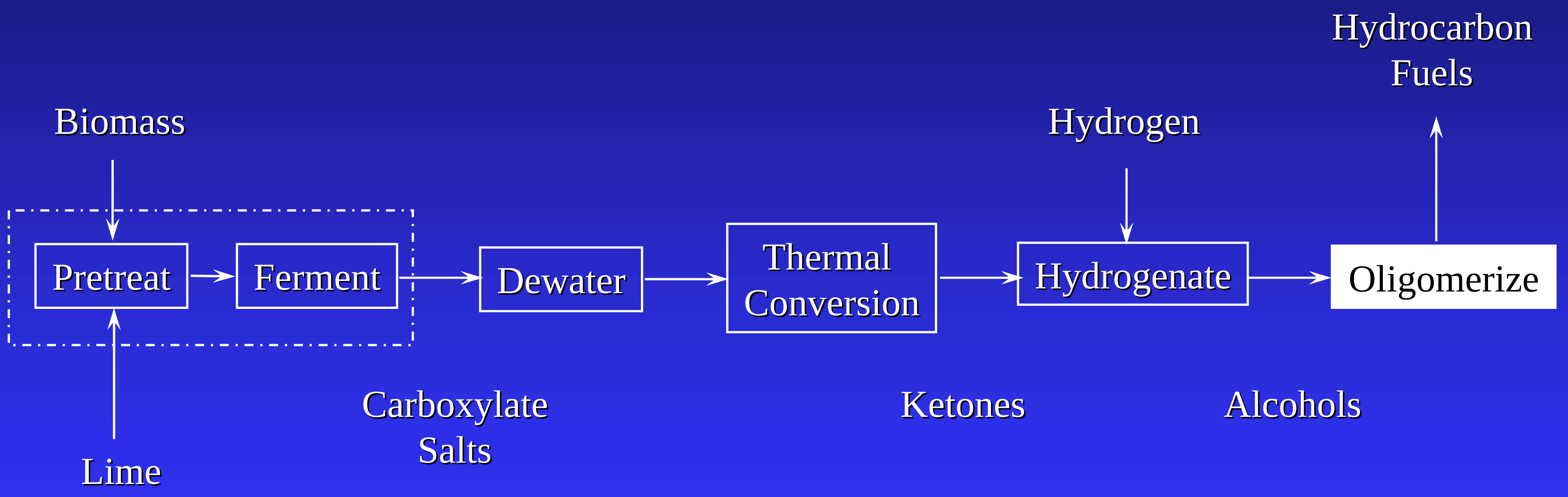
Temperature = 130°C

Time = 35 min (@ P = 15 atm)

Hydrogenation



MixAlco Process



Oligomerizaton Chemistry

Dehydrate

$$H_3C\overset{\displaystyle OH}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}CH_3 \rightarrow H_3CHC{=}CH_2 + H_2O$$

Isopropanol Propylene

Dimerize

$$H_3CHC{=}CH_2 + H_3CHC{=}CH_2 \rightarrow H_3CCH_2CH_2\,HC{=}CHCH_3$$

Propylene Propylene Hexene

Saturate

$$H_3CCH_2CH_2\,HC{=}CHCH_3 + H_2 \rightarrow H_3CCH_2CH_2CH_2CH_2CH_3$$

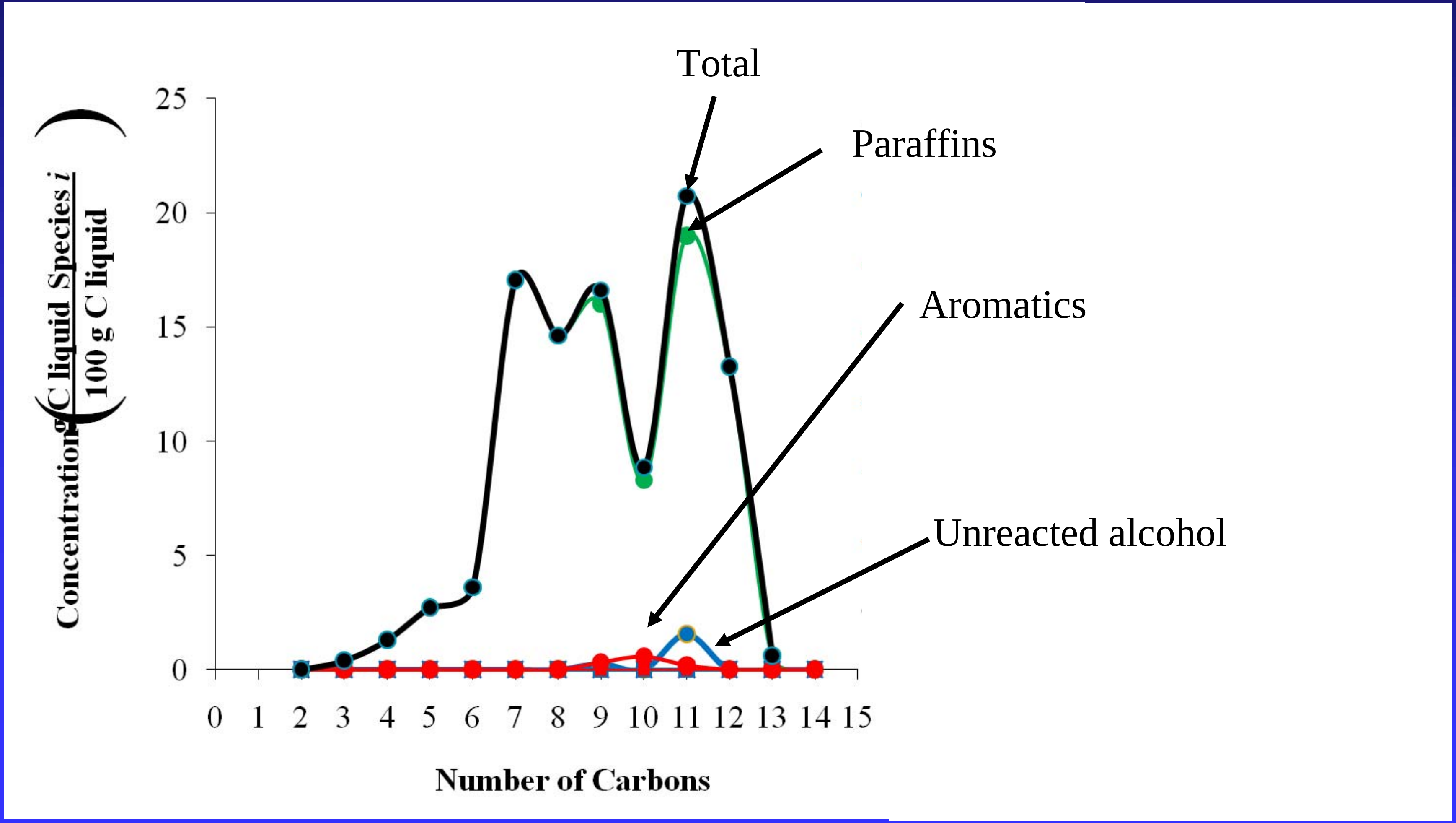
Hexene Hexane

Mixed Alcohols to Hydrocarbons

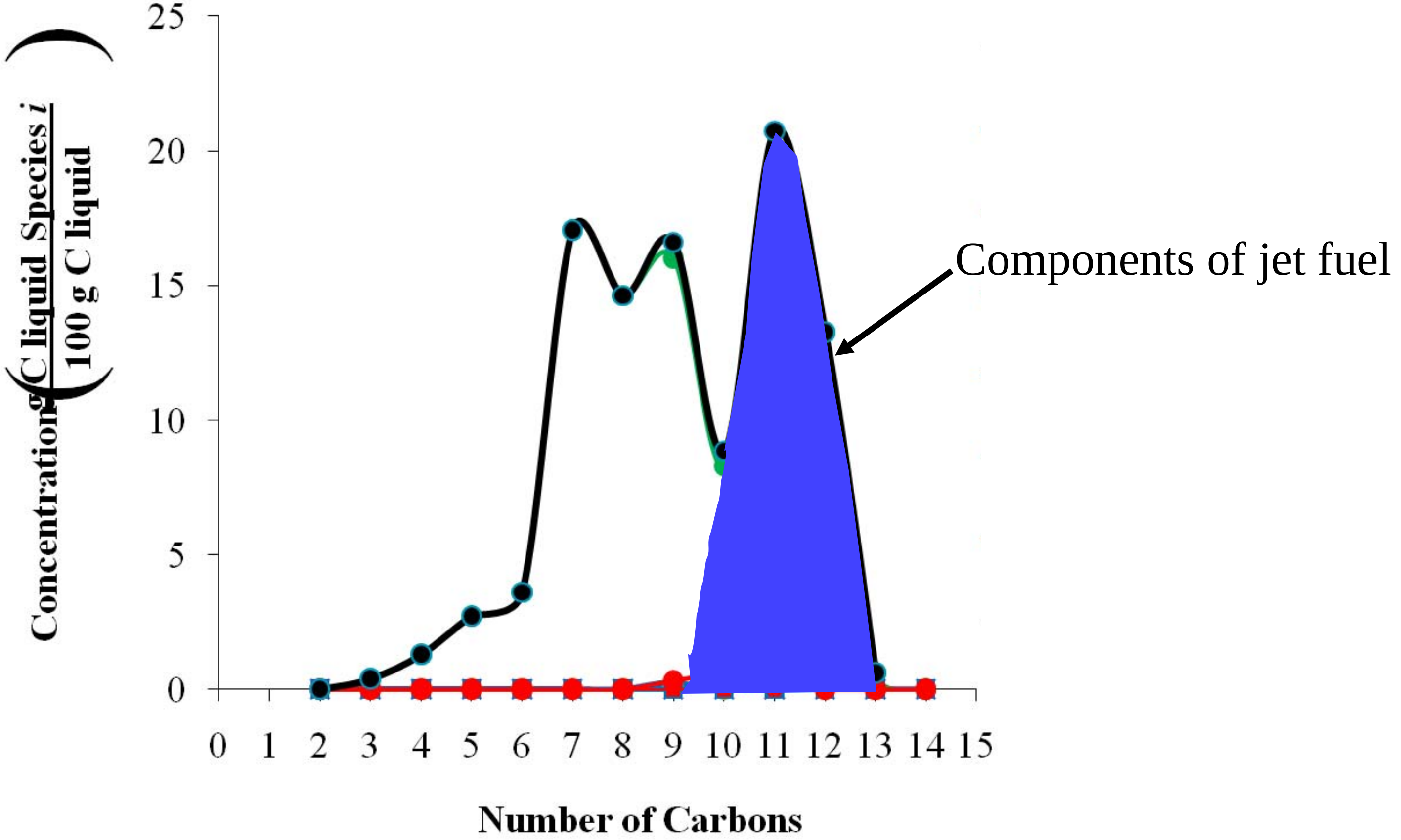
Mixed alcohols
from MixAlco process

Hydrocarbon

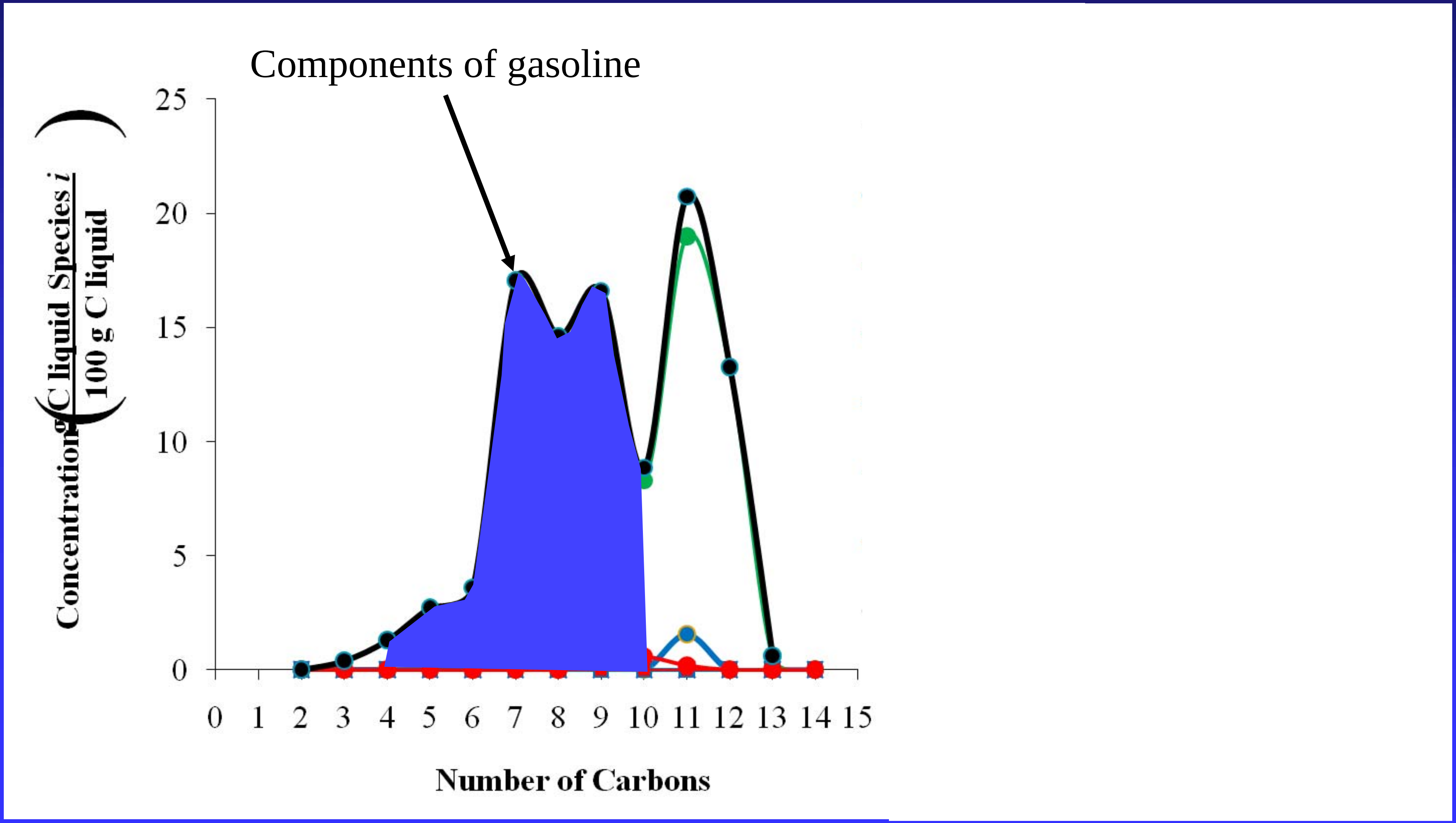
Mixed Alcohols to Hydrocarbons



Mixed Alcohols to Hydrocarbons



Mixed Alcohols to Hydrocarbons



MixAlco Advantages

- Can use wet feedstocks
- Wide range of feedstocks
- Energy efficient
- No genetically modified organisms
- Many products
- Distributed processing

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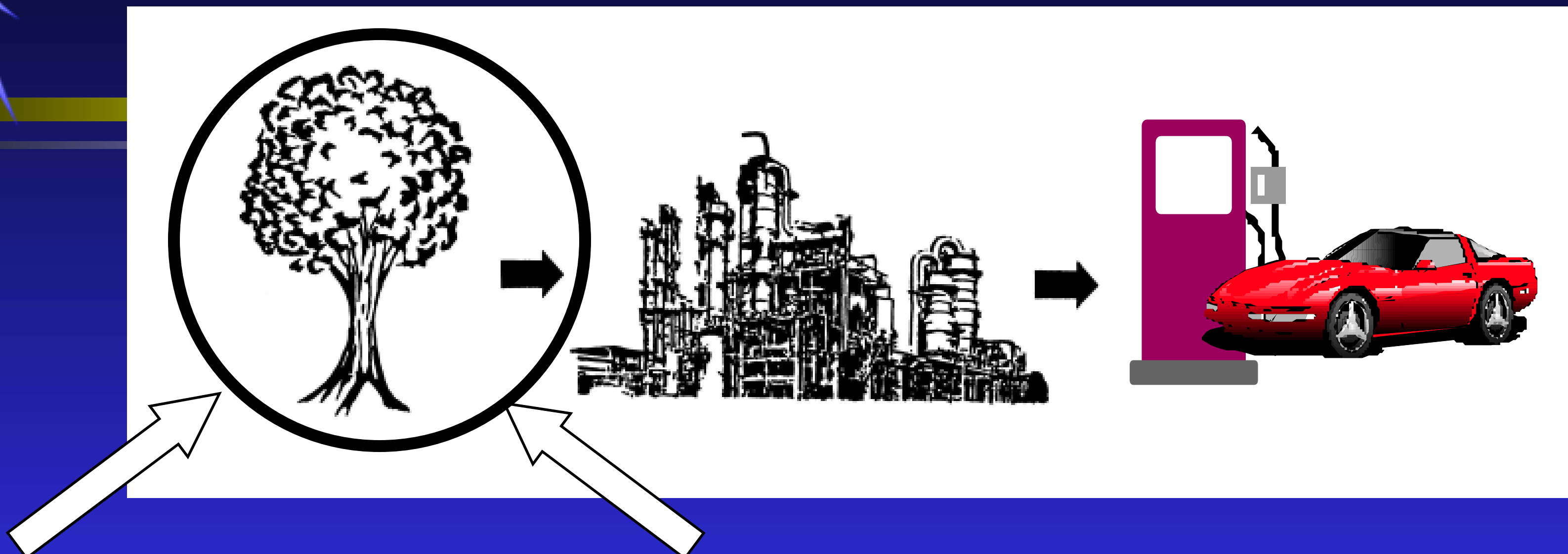
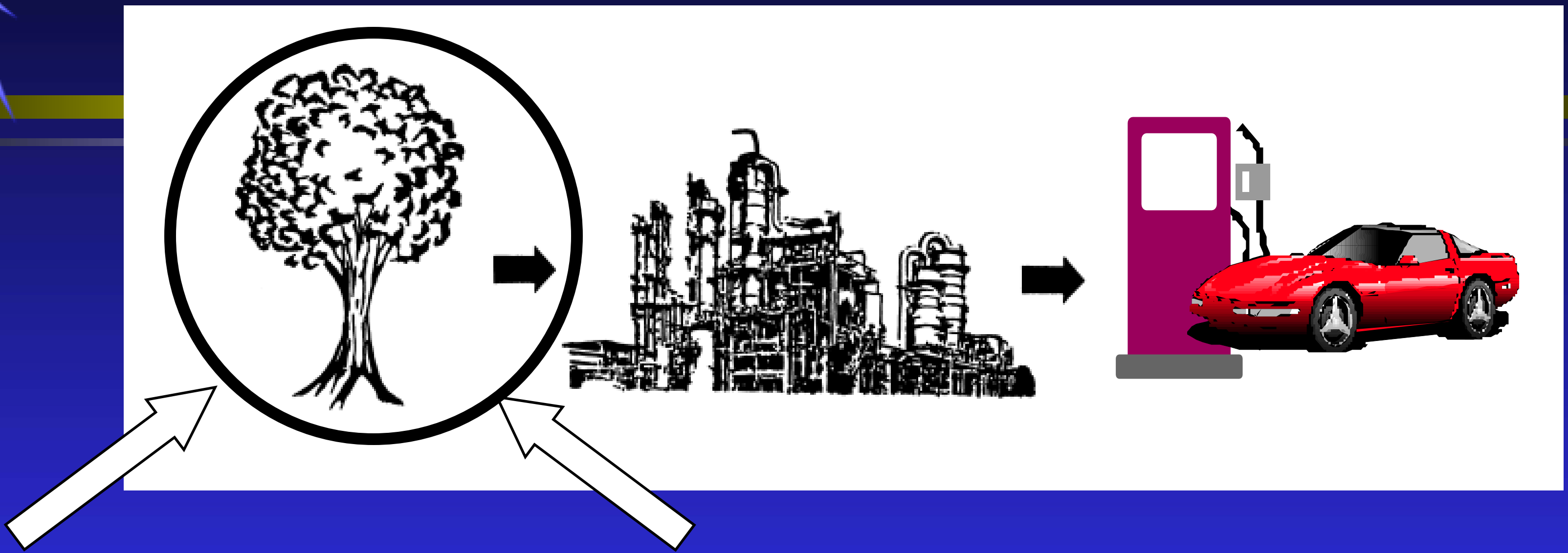
MixAlco Feedstocks



- trees
- grass
- agricultural residues
- energy crops

- animal manure
- sewage sludge
- municipal solid waste
- algae “bodies”

MixAlco Feedstocks



- trees
- grass
- **agricultural residues**
- energy crops
- animal manure
- sewage sludge
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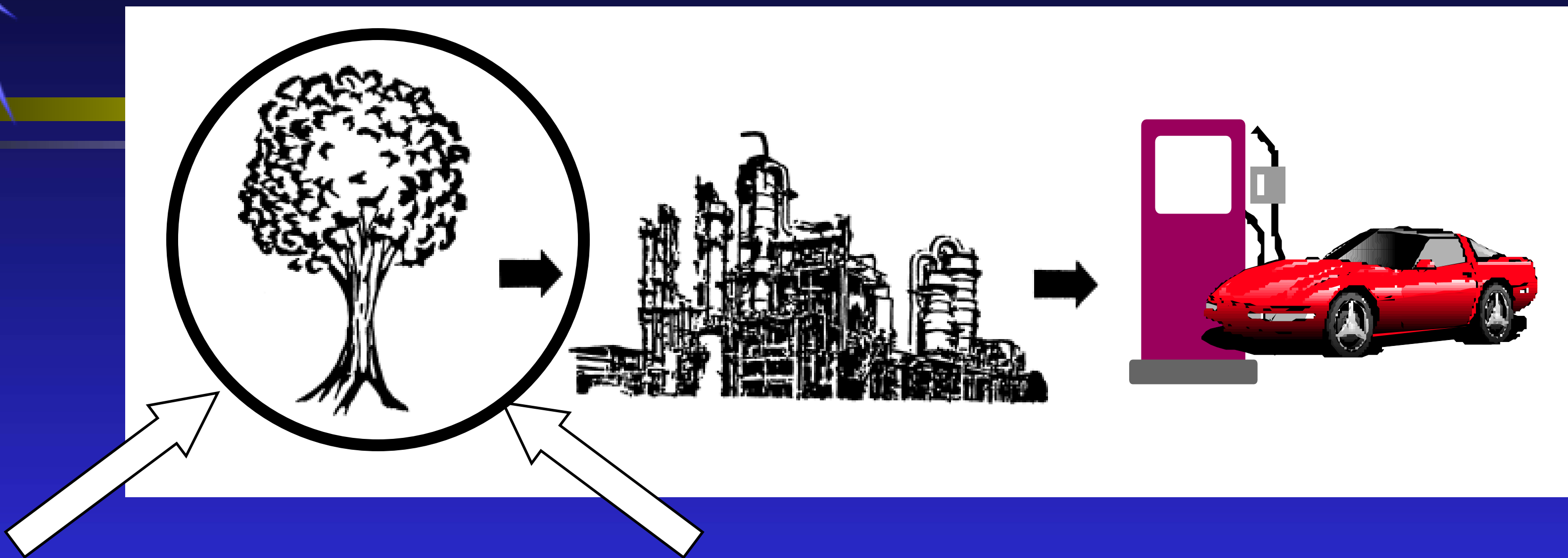
- algae “bodies”

Sugarcane Bagasse

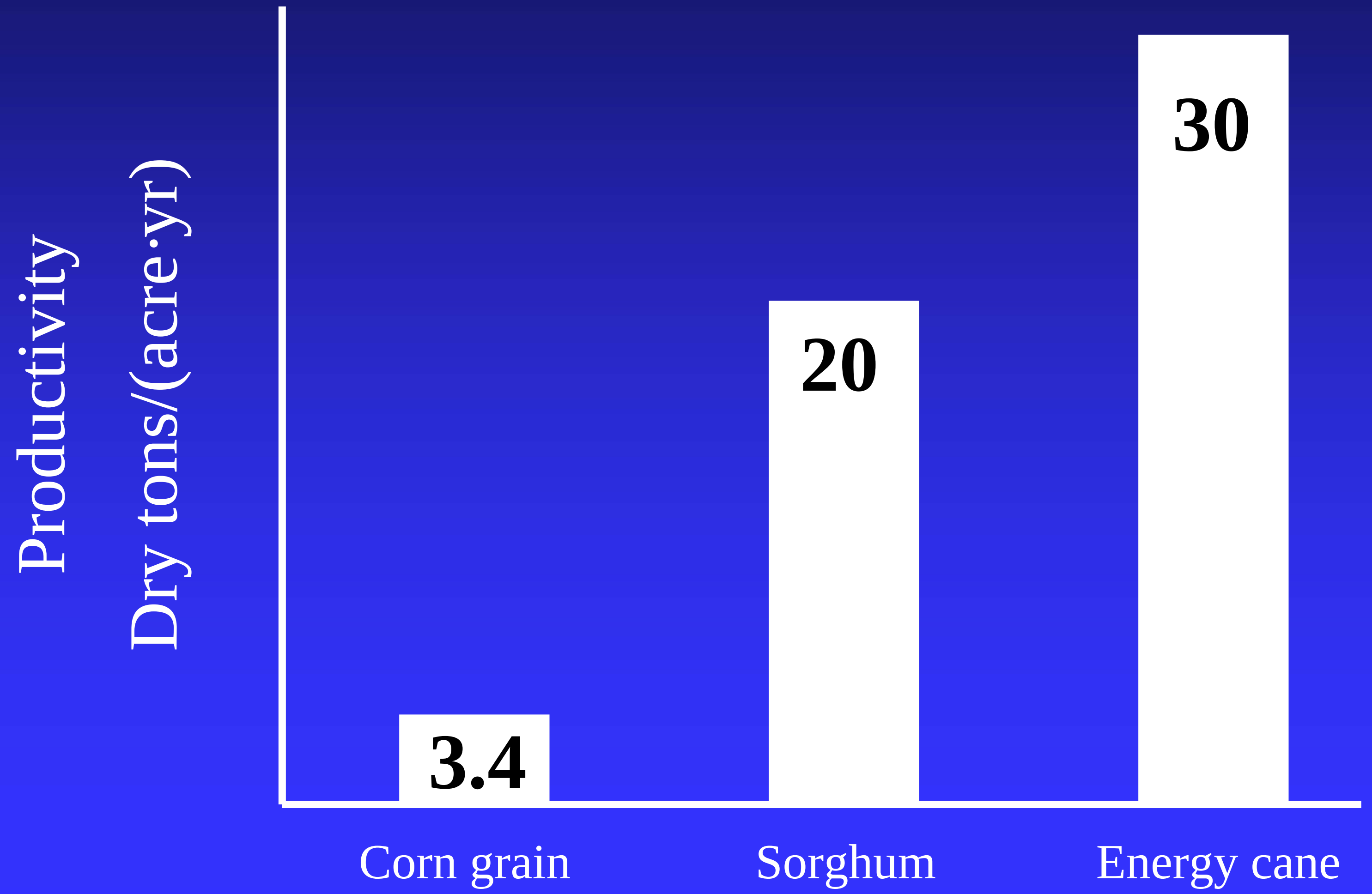
~100 ft

MixAlco Feedstocks

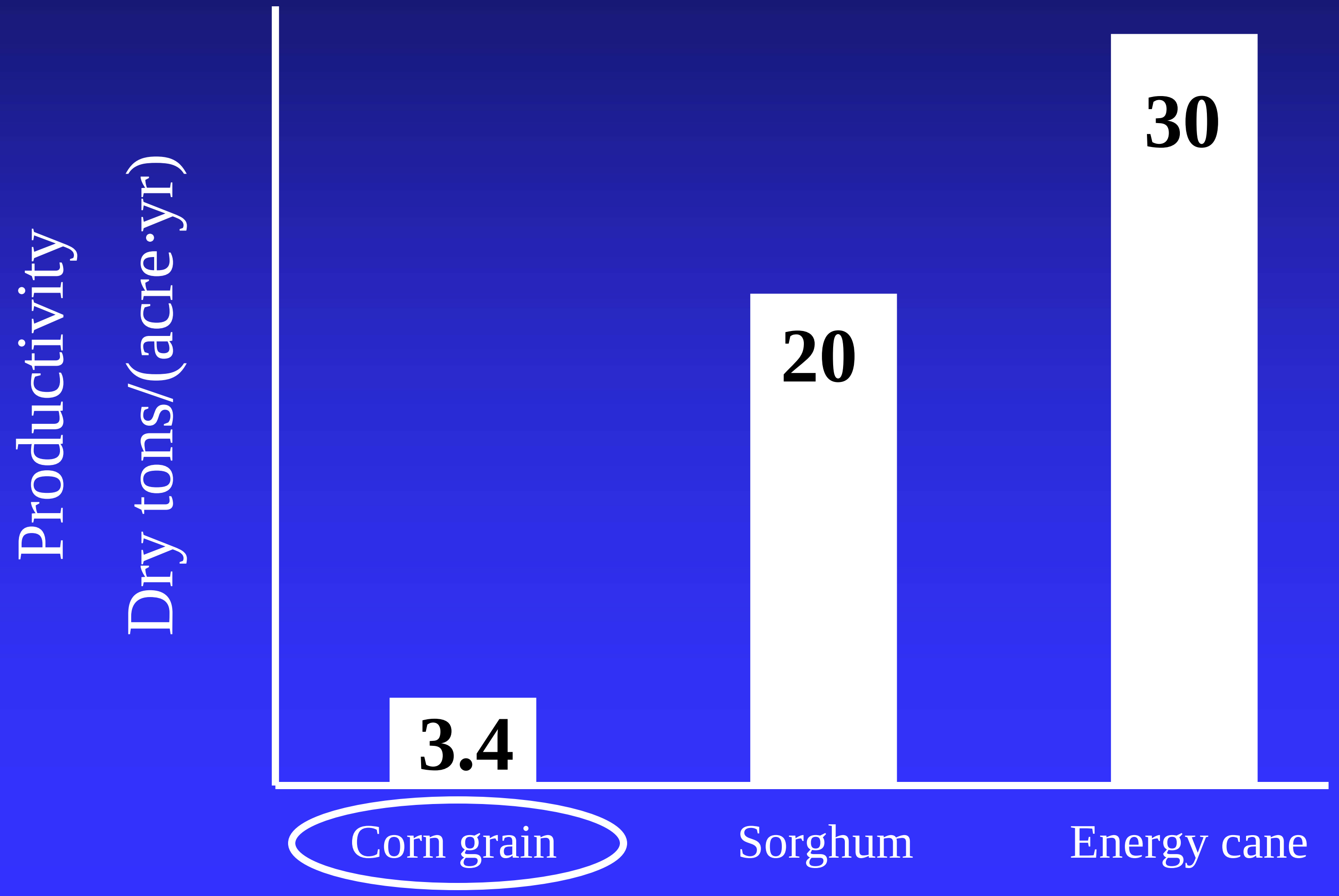


- trees
- grass
- agricultural residues
- **energy crops**
- animal manure
- sewage sludge
- municipal solid waste
- algae “bodies”

Productivity



Productivity



Current-Generation Biofuels

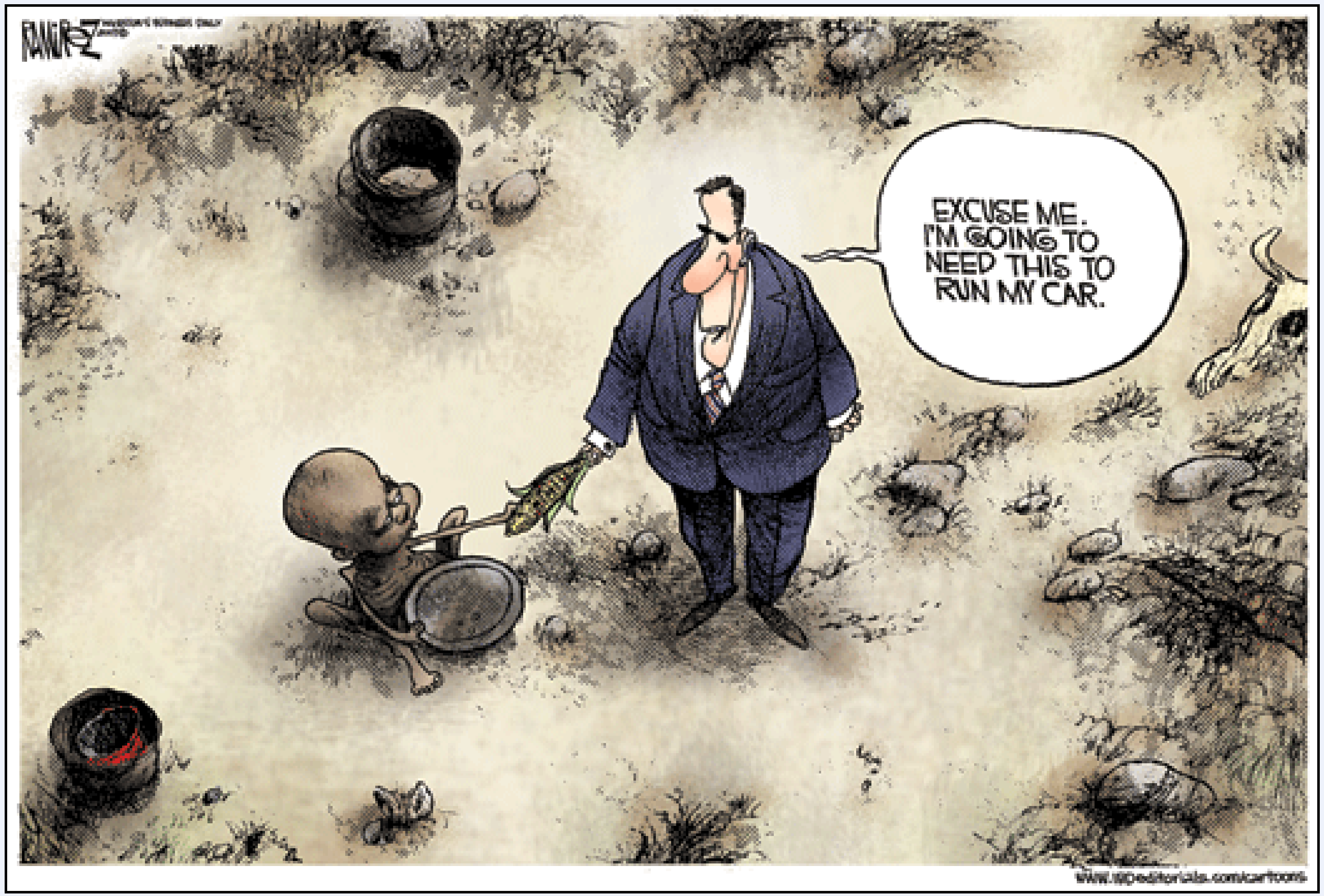
http://petroleum.berkeley.edu/papers/patzek/CRPS416-Patzek-Web.pdf

Cornfield

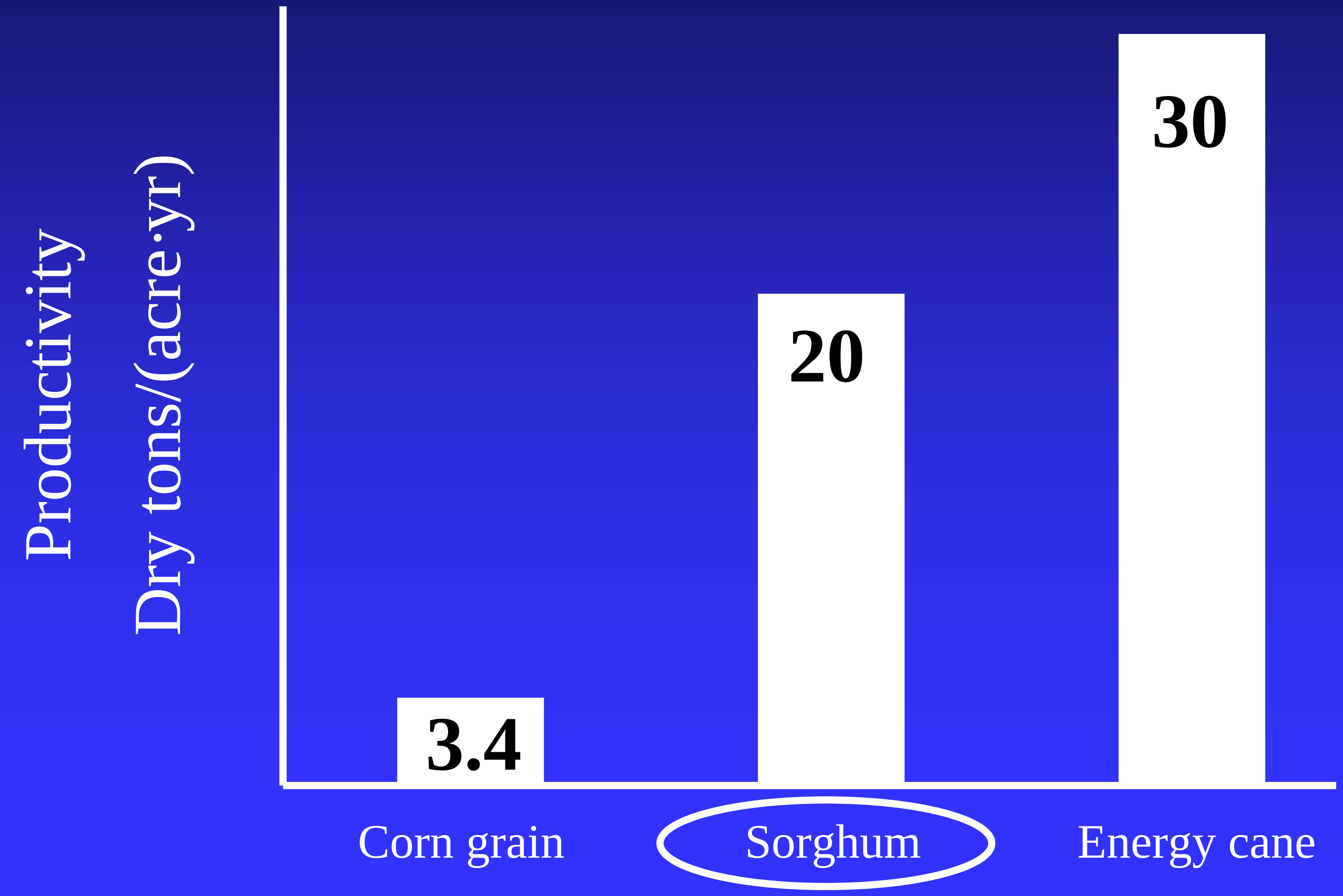
Bart and Phillip

Corn Land Area Required to Supply 100% of US Gasoline

Competition with Food



Productivity



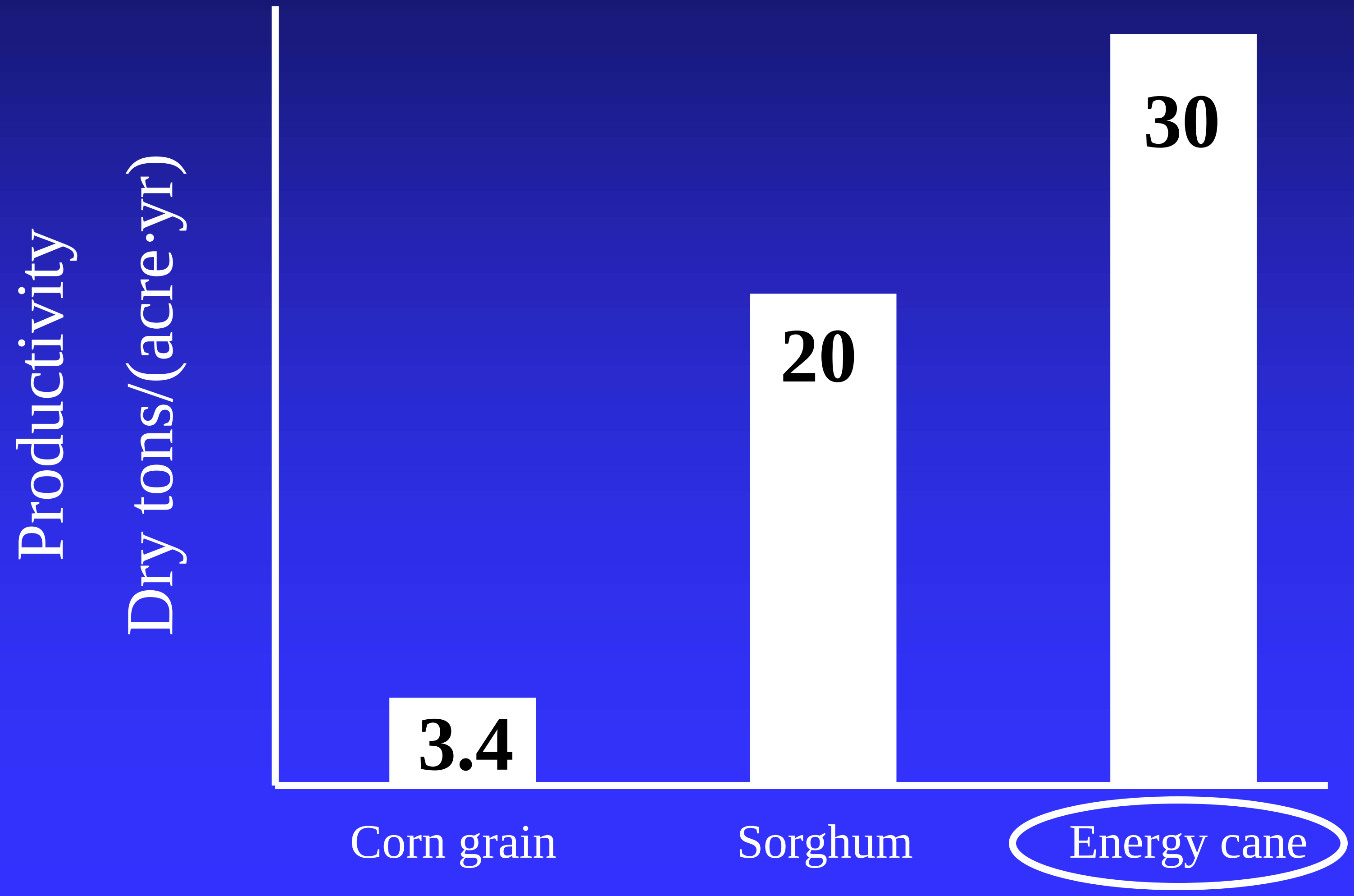
Sorghum

Grows in ~35 US states

Yield = 20–25 dry ton/(acre·yr)

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

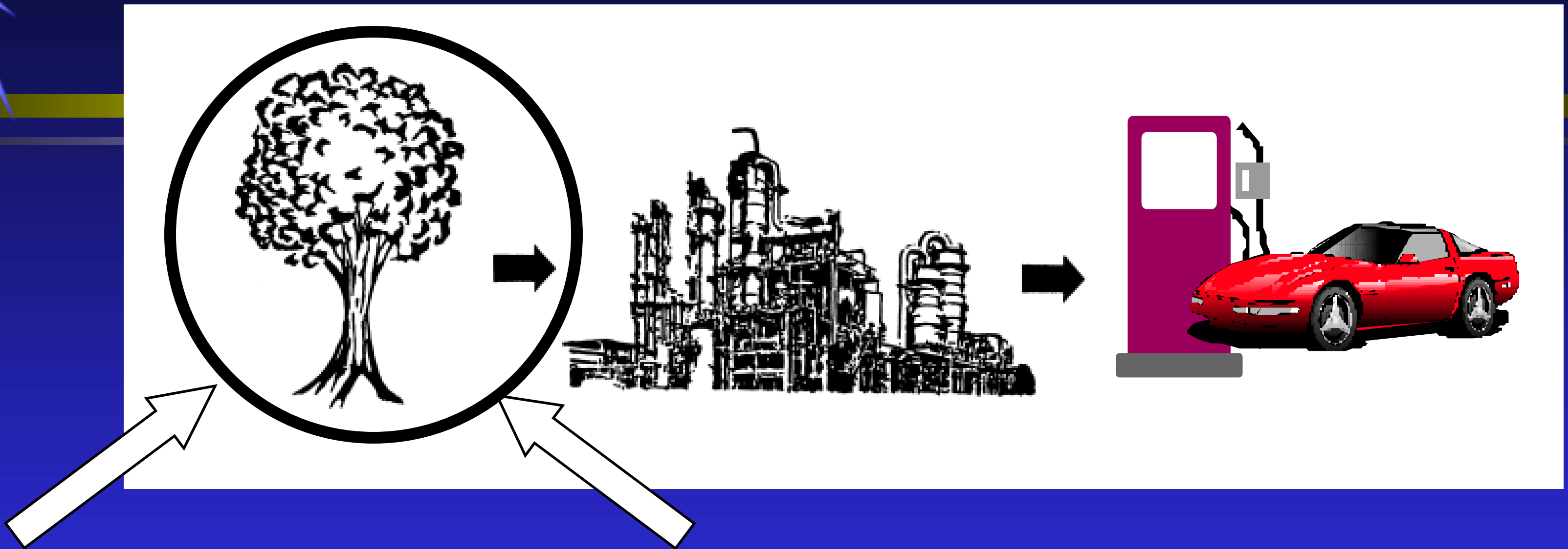
Productivity



Energy Cane

Energy Cane

MixAlco Feedstocks



- trees
- grass
- agricultural residues
- energy crops

- animal manure
- sewage sludge
- **municipal solid waste**
- algae "bodies"


Garbage
Energy Crops

MixAlco Advantages

- Can use wet feedstocks
- Wide range of feedstocks
- Energy efficient
- No genetically modified organisms
- Many products
- Distributed processing

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%)

$$\frac{15.7\text{ MJ heat}}{1000\text{ kg water}} \times \frac{95\text{ kg water}}{5\text{ kg acid}} = \frac{0.3\text{ MJ}}{\text{kg acid}} = \boxed{1.7\%} \text{ of the combustion heat}$$

Work = 5.5 kWh/thous gal = 1.45 kWh/m^3

Assume heat to work is 33% efficient

MixAlco Advantages

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- Wide range of feedstocks
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MixAlco Advantages

- Can use wet feedstocks
- Wide range of feedstocks
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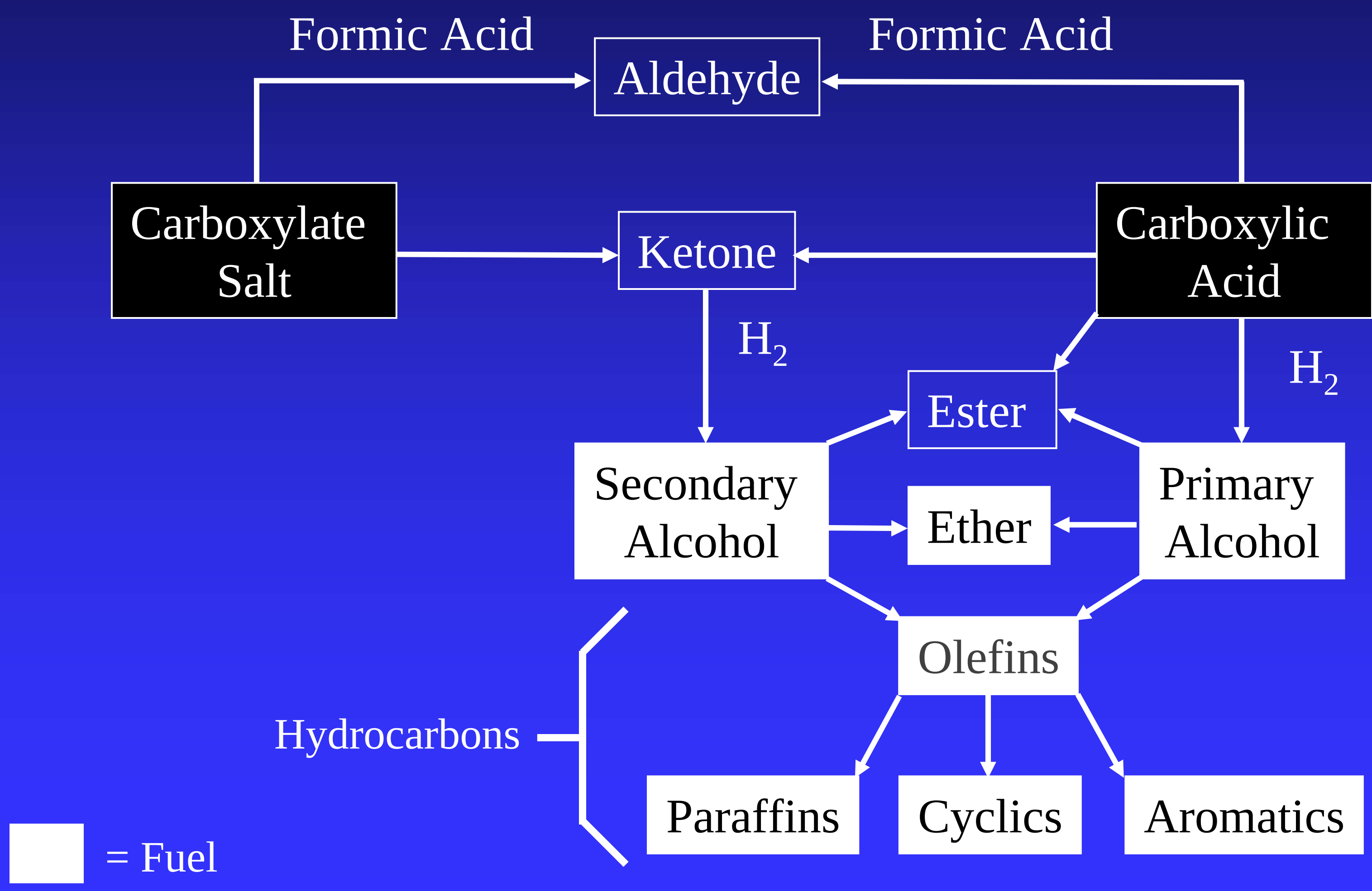
Chemistry

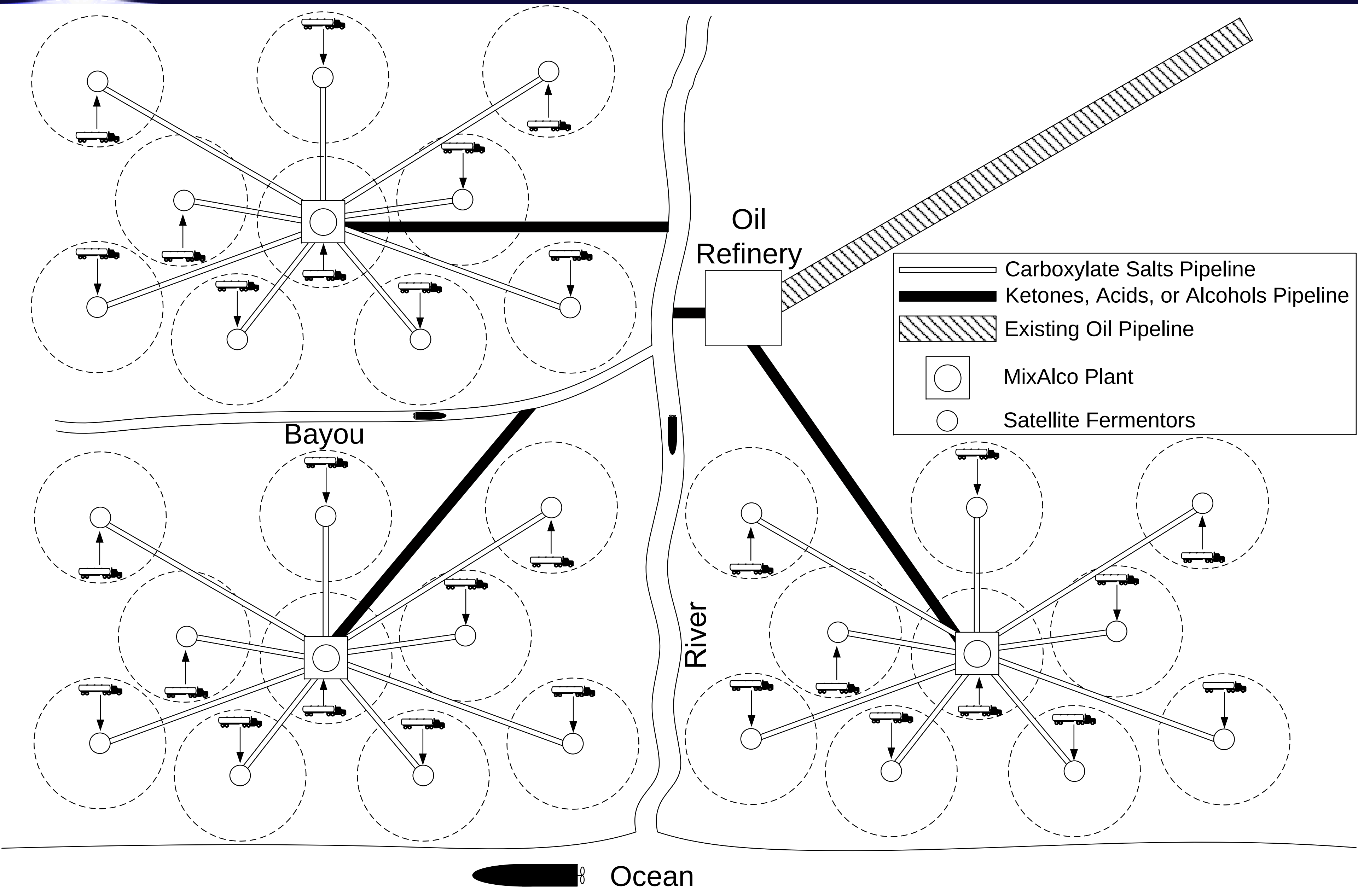


Formic Acid
Aldehyde
Formic Acid
Carboxylate Salt
Ketone
Carboxylic Acid
H_2
H_2
Ester
Secondary Alcohol
Ether
Primary Alcohol
Olefins
Hydrocarbons
Paraffins
Cyclics
Aromatics
= Fuel

MixAlco Advantages

- Can use wet feedstocks
- Wide range of feedstocks
- Energy efficient
- No genetically modified organisms
- Many products
- Distributed processing

MixAlco Logistics (Example)



MixAlco Advantages

No Enzyme Addition

MixAlco Advantages

No
Sterility

Economics

Economics

Competes with oil at about $70/bbl without subsidies

Brief History of MixAlco Process

1991 – Laboratory research began

2000 – Pilot plant construction began

2008 – Demonstration plant construction begins

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Brief History of MixAlco Process

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TERRABON

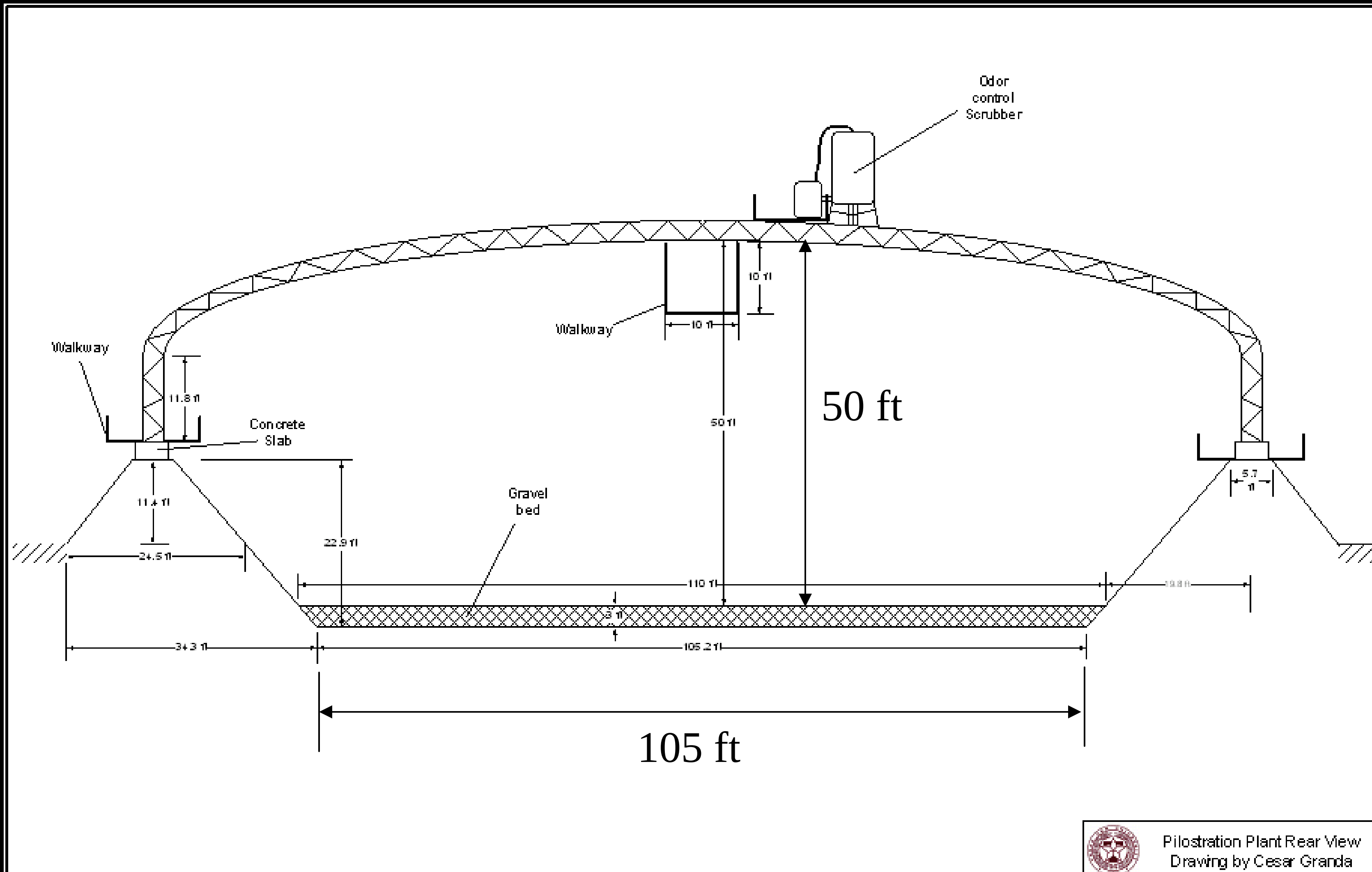
Brief History of MixAlco Process

1991 – Laboratory research began

2000 – Pilot plant construction began

2008 – Demonstration plant construction began

Fermentor Structure



Construction has begun!!

Construction

Construction

Construction

Construction

Construction

Construction

Fermentor Interior

Completed Fermentor

Giant Cattle Rumen

Dedication (November 2008)

Governor Speaking

Holtzapple Speaking

Naming the Demonstration Plant

Holtzapple Family with Governor

Holtzapples with Governor

Outline

- Background
- Biofuels
- Advanced Engines

Sorghum Land Area

Conventional Car

30 mpg*

* at 70 miles per hour

$$\eta_{comp} = \eta_{exp} = 82\%$$

$$\Downarrow$$

$$\eta_{engine} = 57 - 66\%$$

STAR ROTOR Corporation

Sorghum Land Area

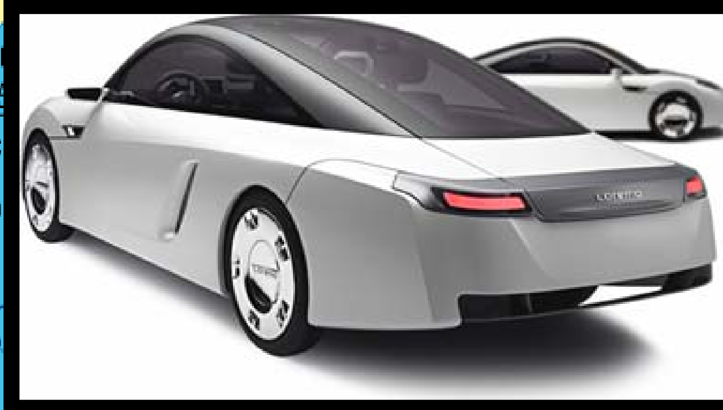
StarRotor Engine

90 mpg*

* at 70 miles per hour

Sorghum Land Area

Loremo
with
StarRotor Engine



235 mpg*

* at 70 miles per hour

Sorghum Land Area

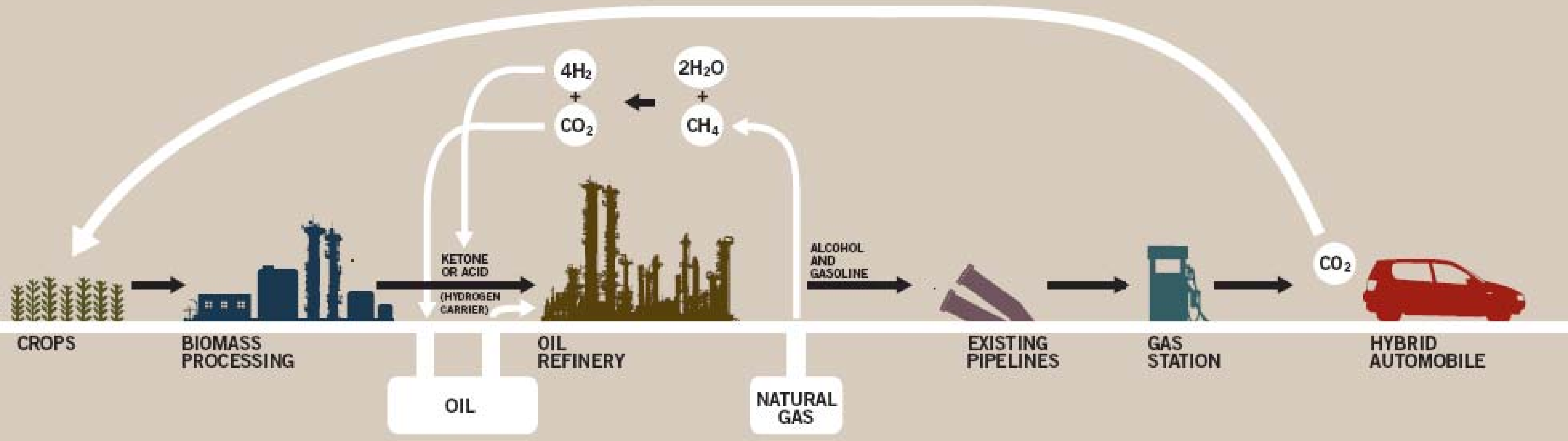
Aptera
with
StarRotor Engine

380 mpg*

* at 70 miles per hour

Aptera

Aptera



Thank you for your time and attention