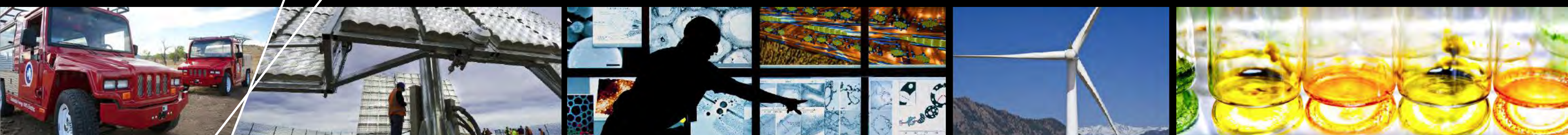
# Realizing the Potential of Advanced BioFuels




**Thomas D. Foust, Ph.D., P.E.**
**Director,**
**National Advanced Fuels Consortium**


**June 14, 2012**

# National Advanced Fuels Consortium

NABC National Advanced Biofuels Consortium

*Biofuels for Advancing America*

**Project Objective** – Develop cost-effective technologies that supplement petroleum-derived fuels with advanced "drop-in" biofuels that are compatible with today's transportation infrastructure and are produced in a sustainable manner.

**3 year effort - $50M/year**

**Consortium Partners**

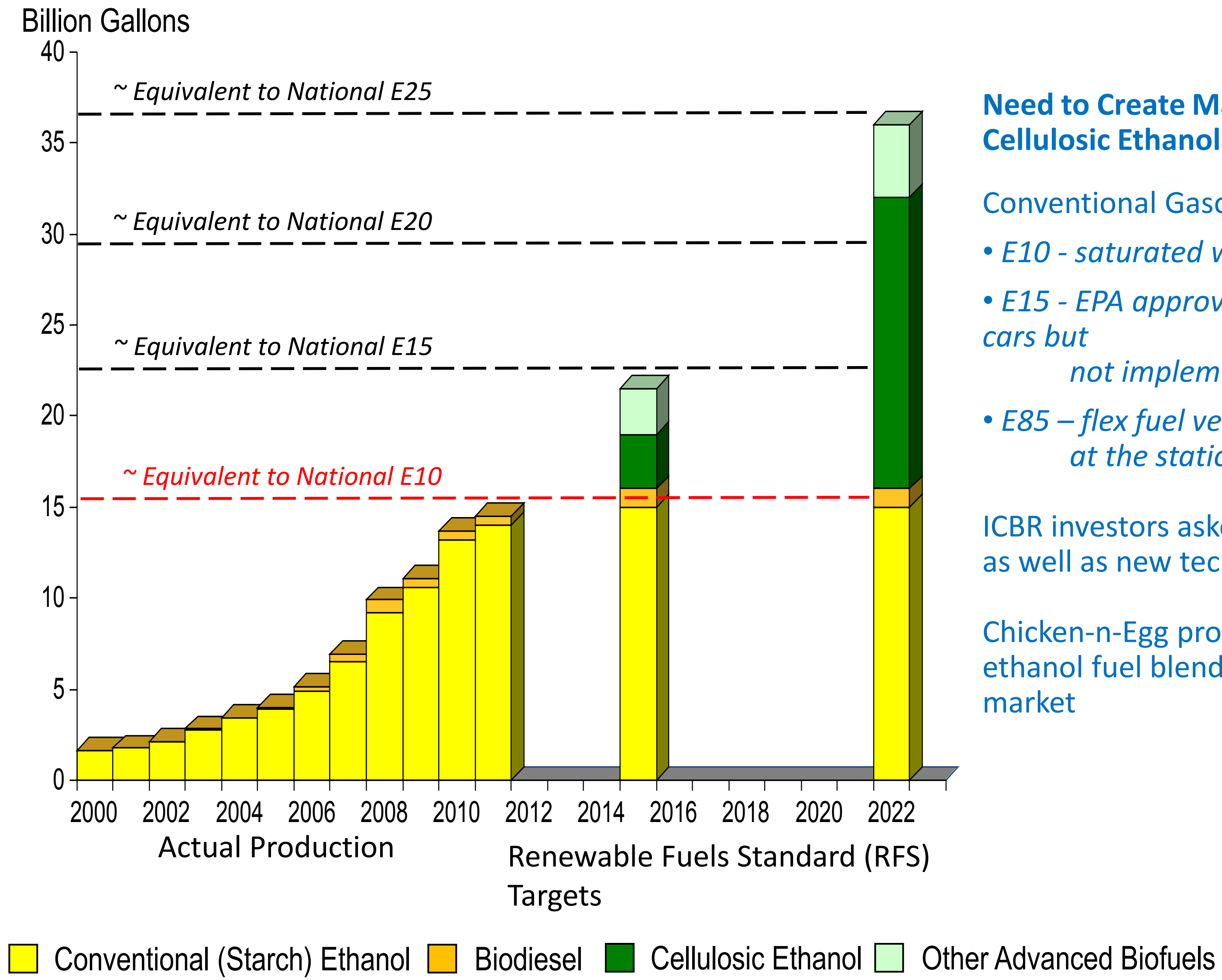
Albemarle Corporation
Amyris Biotechnologies
Argonne National Laboratory
BP Products North America Inc.
Catchlight Energy, LLC
Chevron
Colorado School of Mines
General Motors
Honda
Iowa State University
Los Alamos National Laboratory
National Renewable Energy Laboratory
Oakridge National Laboratory
Pall Corporation
RTI International
Tesoro Companies Inc.
University of California, Davis
UOP, LLC
Virent Energy Systems
Washington State University

# 2011 EIA Crude Oil Price Projections

Figure 5. Average annual world oil prices in three cases, 1980-2035

(real 2010 dollars per barrel)

# Marketplace for Renewable Fuels




**Need to Create Market Demand for Cellulosic Ethanol**

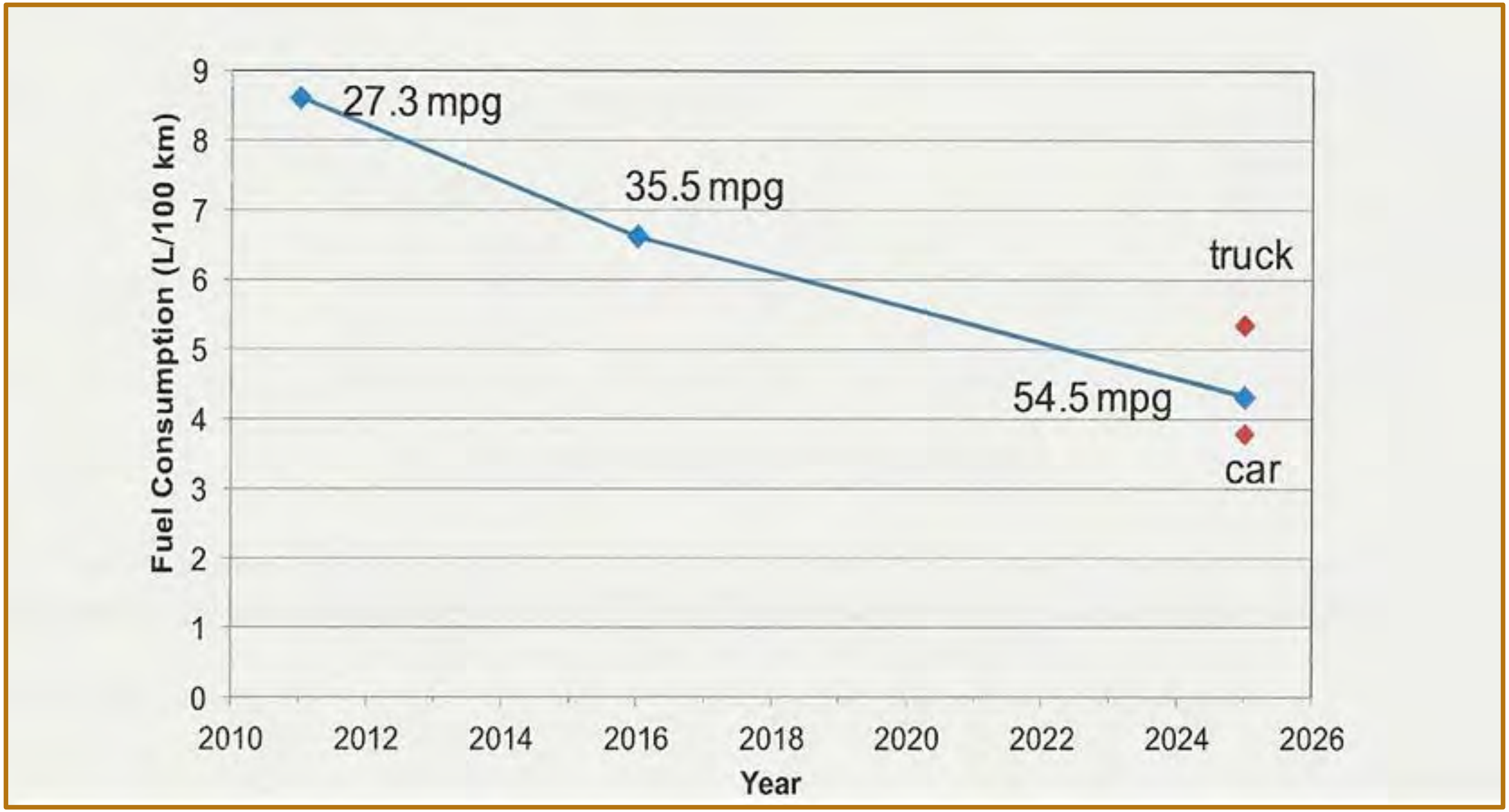
Conventional Gasoline

- *E10 - saturated with corn ethanol*
- *E15 - EPA approved for 2001 and newer cars but not implemented in the field*
- *E85 – flex fuel vehicles grew but fuel at the stations never materialized*

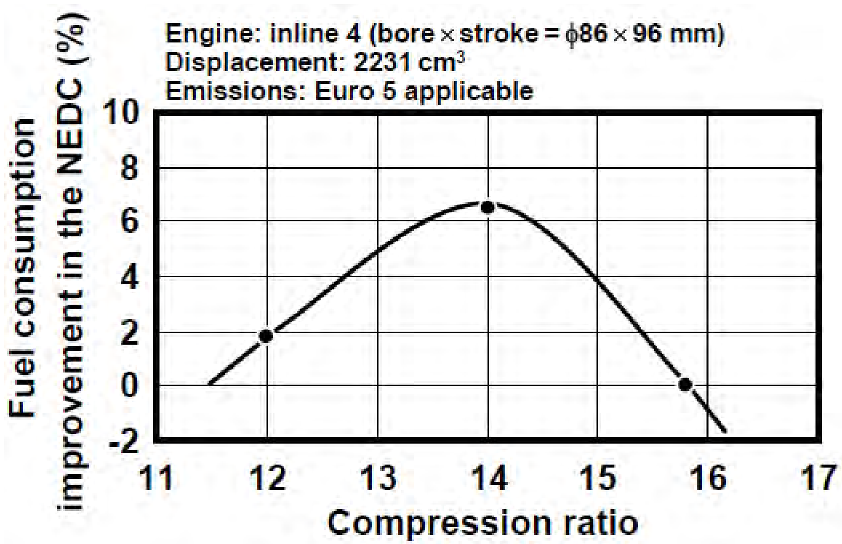
ICBR investors asked to take on market risk as well as new technology risks

Chicken-n-Egg problem between high ethanol fuel blends and vehicles in the market

# Proposed Fuel Economy Legislation – Current through 2025

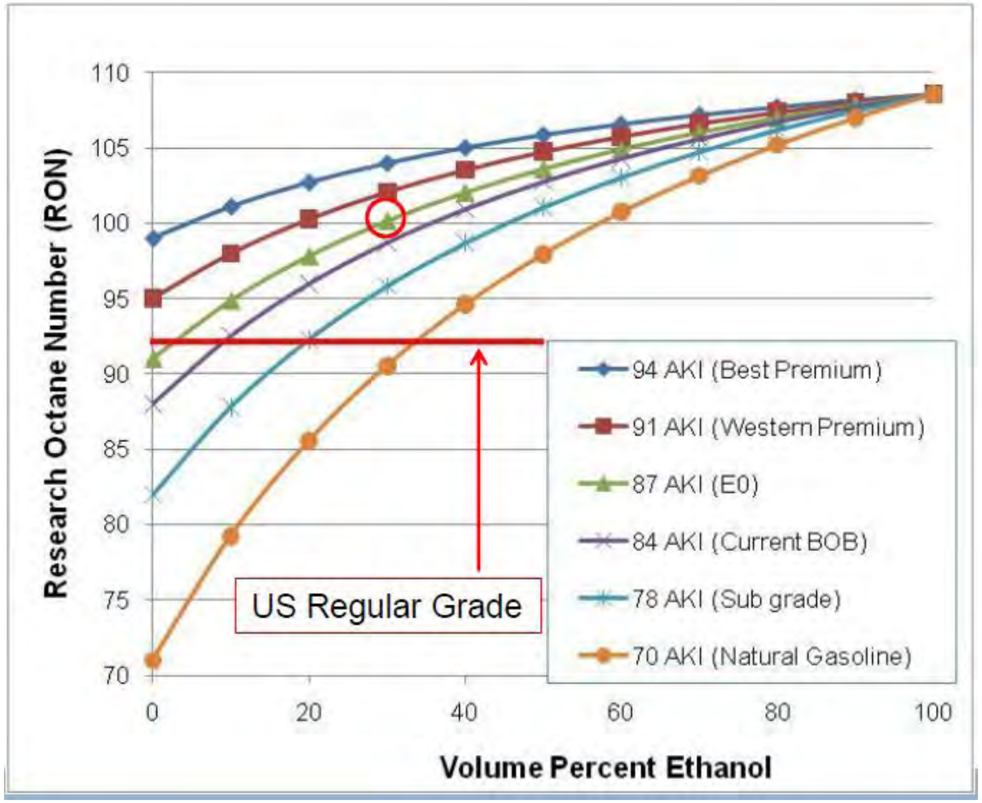


# Ethanol Can Enable More Efficient Engines




- Higher compression ratio yields higher efficiency
- Above CR of 14 piston ring friction dominates
- CR=14 is optimal
- Current engine CR about 10

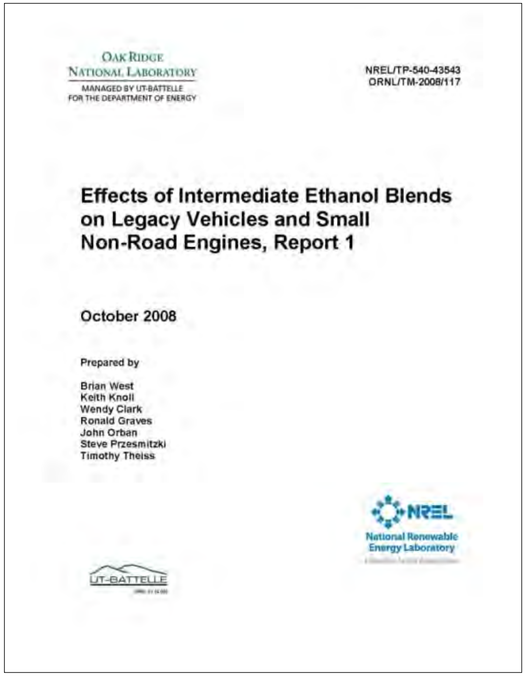
- **Higher CR would be enabled by HIGHER Octane Number**
  - Ethanol has a much higher blending Octane Number than hydrocarbon blendstocks
  - Another advantage of ethanol is cooling effect of vaporization – much greater than hydrocarbon



# Ethanol

## Ethanol market

- **EPA has approved E15 as substantially similar to gasoline for 2001 and newer models**
  - Currently be rolled out state by state
  - Car manufacturers need higher octane specially high RON low MON  to meet new café standards
    - mid level ethanol blends are a cost effective manner to achieve this
    - High RON low MON benefits to E25
    - Butanol also good for high RON low MON
    - Likely to start approving models in model year 2012 with more to follow in 2013 and 2014
  - Small engines, pumps and dispensers remain an unresolved issue
  - RFA aggressively working these issues and is strongly committed to E15
- **E85 volumes gaining slightly but still very small as overall percentage of ethanol volumes**
- **VETC (ethanol tax credit) phased out on January 1, 2012**
  - Effect on EtOH production difficult to ascertain


OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

NREL/TP-540-43543
ORNL/TM-2008/117

Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines, Report 1

October 2008

Prepared by

Brian West
Keith Knoll
Wendy Clark
Ronald Graves
John Orban
Steve Przesmitzki
Timothy Theiss

NREL National Renewable Energy Laboratory

UT-BATTELLE

# U.S. Transportation Fuel Demand – gasoline use dropping rapidly

**Gasoline* (Finished Motor Gasoline – E10) (cars & trucks)**

**126 bgy**

* Peaked in 2004 at 136 bgy

**Diesel (on-road, rail)**

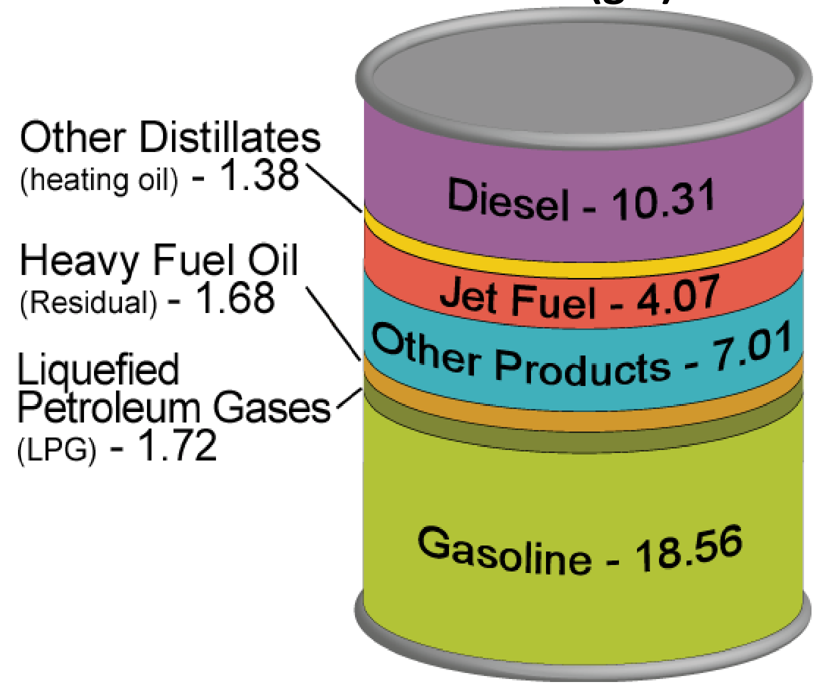
**43 bgy**

**Aviation (jet fuel)**

**23 bgy**

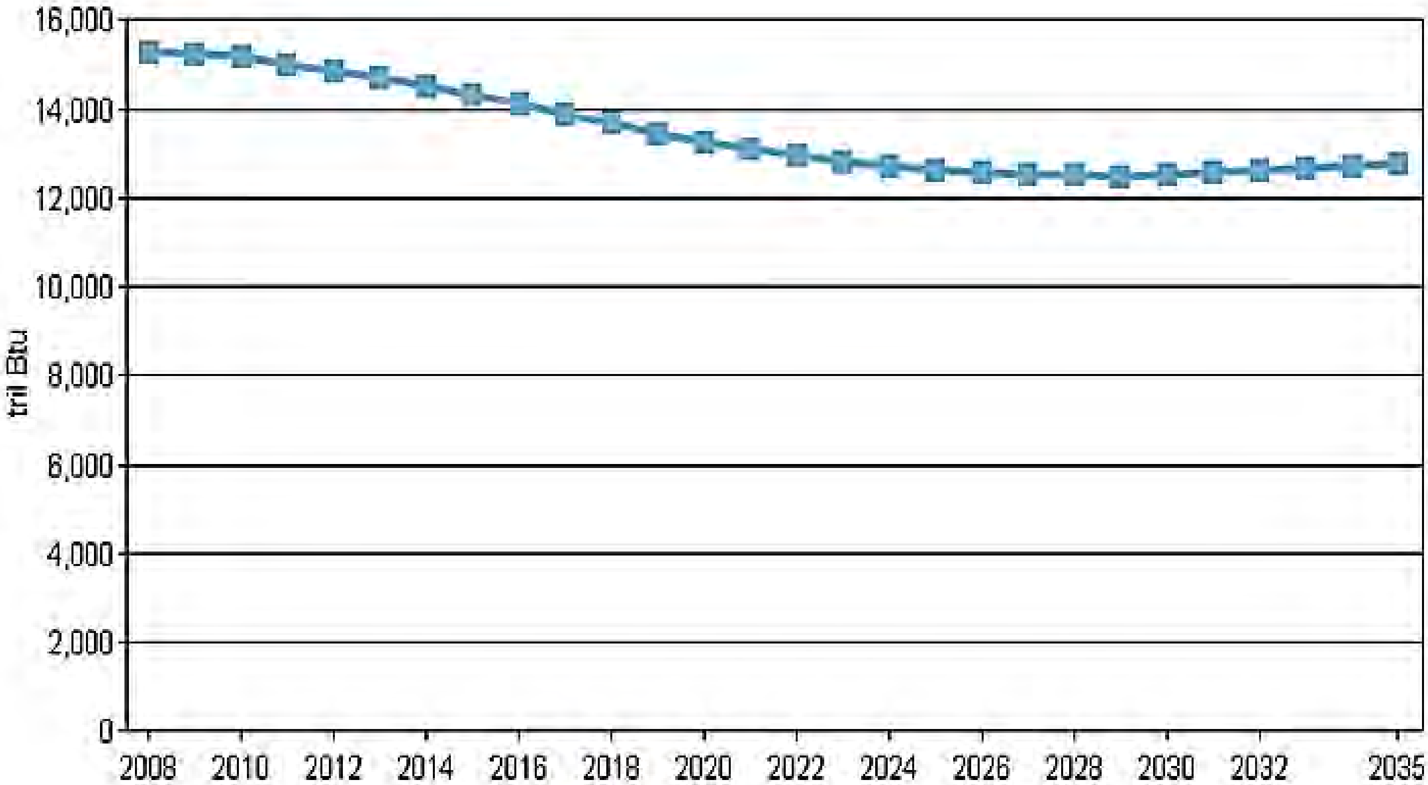
| | 2010 | 2035 |
|---|---|---|
| Gasoline | 126 | 116 |
| Diesel | 43 | 52 |
| Jet fuel | 23 | 27 |

**Products in a Barrel of Crude (gal)**




Source: Energy Information Agency

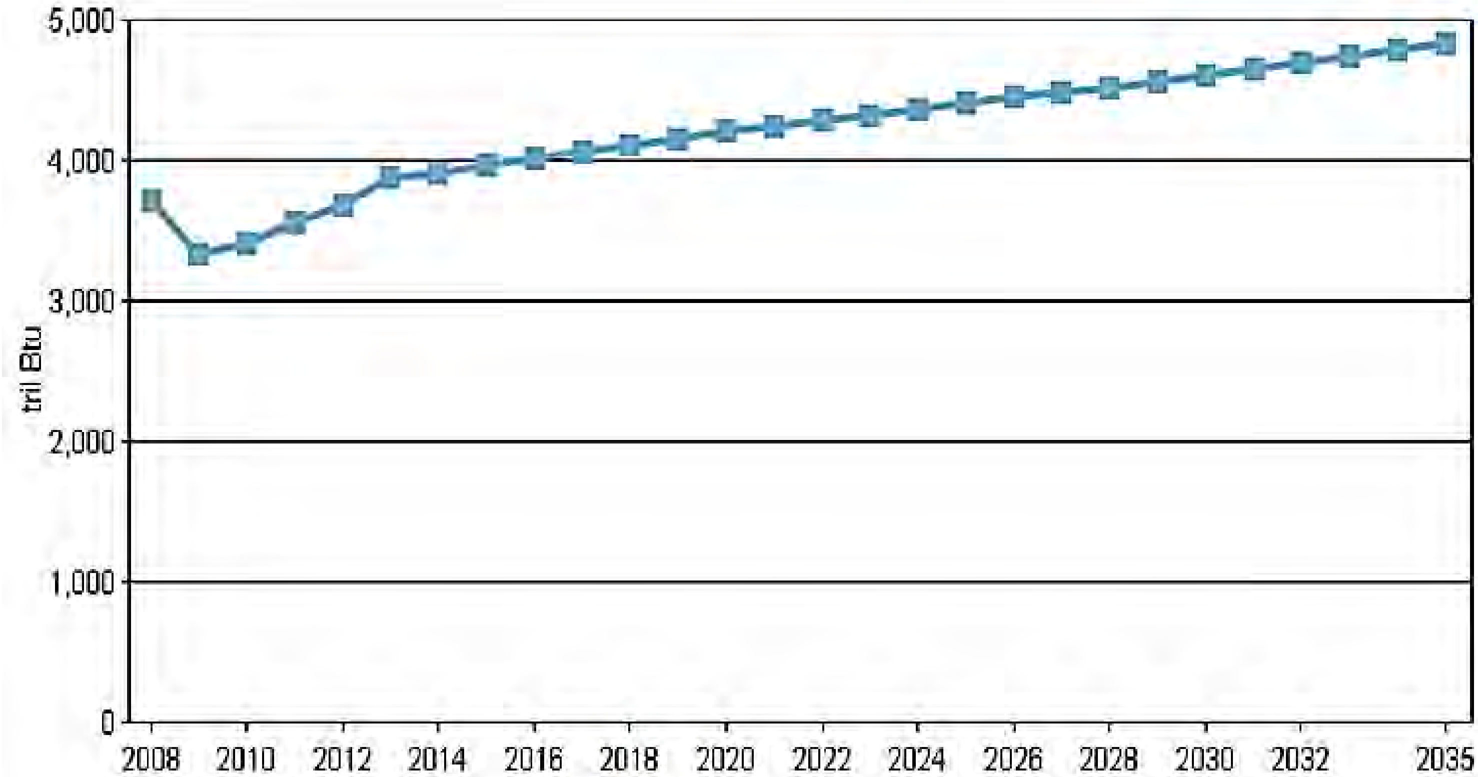
# Transportation Energy Use – Light-Duty Vehicles:
## Conventional Gasoline: Reference Case



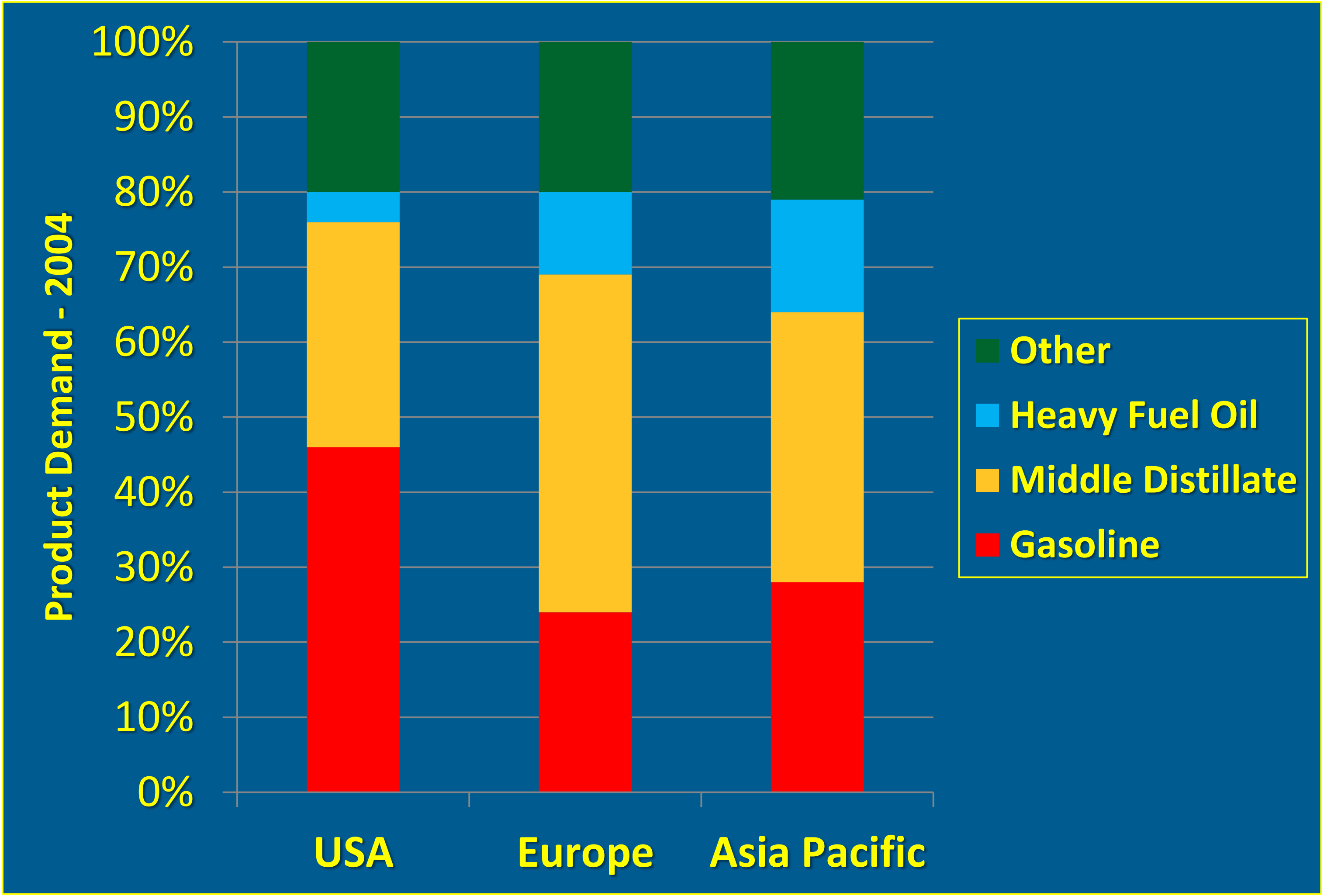

U.S. Energy Information Administration

# Transportation Energy Use – Heavy-Duty Existing Trucks

## Diesel: Reference Case



# US Refining System Is Built To Meet Gasoline Demand




BP Statistical Review of World Energy June 2005

**With all of the technological improvements to gasoline and diesel engines in the past 20 years and what will be required to meet CAFÉ standards, is our current fuels menu optimum for maximizing fuel economy ?**

# US GASOLINE POOL - RON

| Year | Pool RON | Avg. EtOH % | HC Pool RON |
|---|---|---|---|
| 1990 | 93.2 | 1 | 92.1 |
| 2000 | 92.8 | 1.5 | 91.0 |
| 2010 | 92.9 | 8.6 | 82.6 |

# US GASOLINE SALES BY GRADE – % OF TOTAL

| Year | Regular | Mid Grade | Premium |
|---|---|---|---|
| 1990 | 69 | 9 | 22 |
| 2000 | 79 | 7 | 14 |
| 2010 | 88 | 3 | 9 |

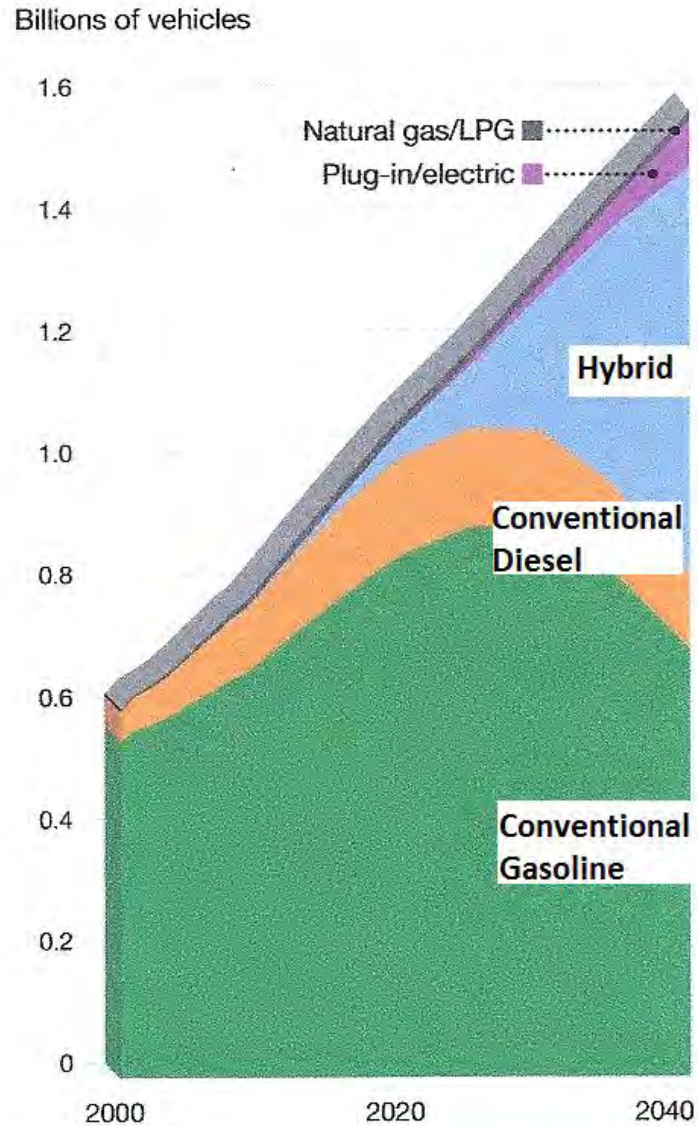
US EIA/Petroleum Marketing Monthly, Feb. 2012

# Ethanol Prices – April 2012

| | Prices | NL | E85 | E10 | E15 | E30 |
|---|---|---|---|---|---|---|
| Gasoline | **$3.3500** | $3.3500 | $1.0050 | $3.0150 | $2.8475 | $2.3450 |
| Ethanol | **$2.1300** | | $1.4910 | $0.2130 | $0.3195 | $0.6390 |
| Product Cost | | $3.3500 | $2.4960 | $3.2280 | $3.1670 | $2.9840 |
| Fed Tax - Gas | $0.1840 | $0.1840 | $0.1840 | $0.1840 | $0.1840 | $0.1840 |
| VEETC - Ethanol | $0.0000 | | $0.0000 | $0.0000 | $0.0000 | $0.0000 |
| State Tax | $0.2800 | $0.2800 | $0.2800 | $0.2800 | $0.2800 | $0.2800 |
| TOTAL COST | | **$3.8140** | **$2.9600** | **$3.6920** | **$3.6310** | **$3.4480** |

RFA RENEWABLE FUELS ASSOCIATION

# Light Duty Vehicle by Fleet Type

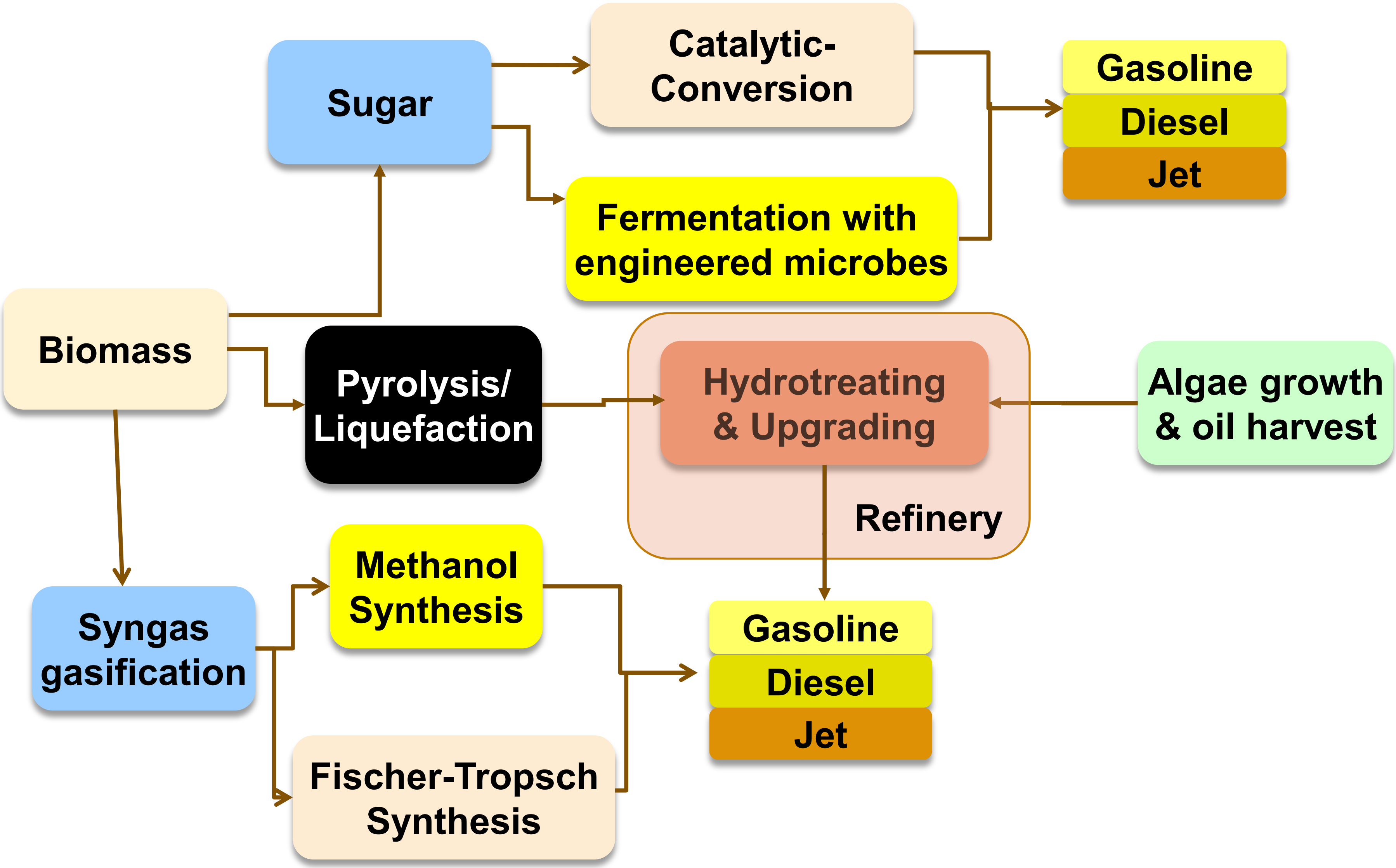



*Exxonmobil.com/energyoutlook*

# TECHNOLOGIES FOR IMPROVING FUEL ECONOMY and REDUCING PETROLEUM IMPORTS

- Partial Hybrids, Hybrids and Plug-in Hybrids
- Electrics
- Extended Range Electrics
- Fuel Cell Vehicles
- Biofuels
- Alternative Fuels
- Low Temperature Combustion
- Diesel Engines
- Improved SI Engines/Transmissions

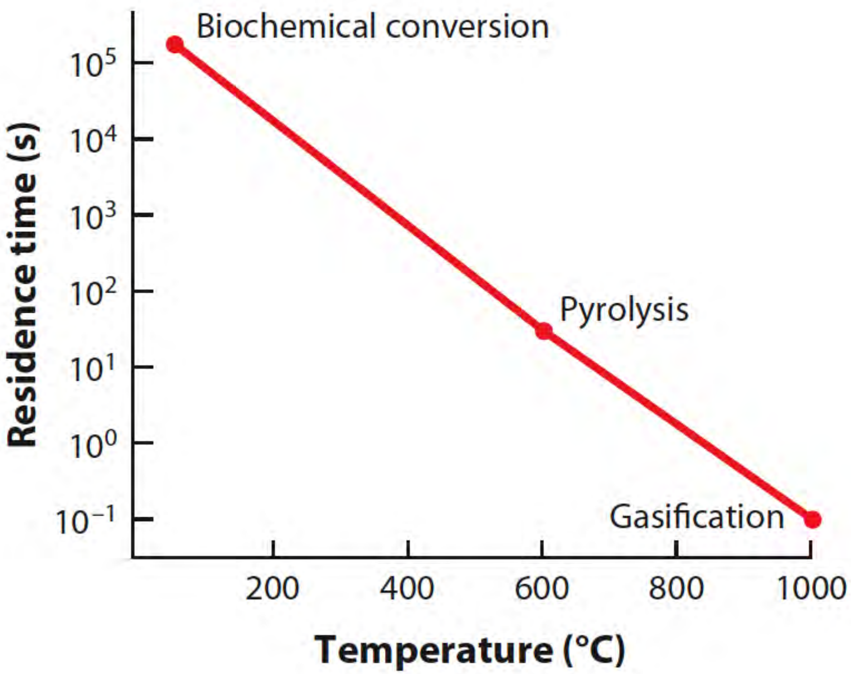
# Advanced Biofuel Conversion Routes

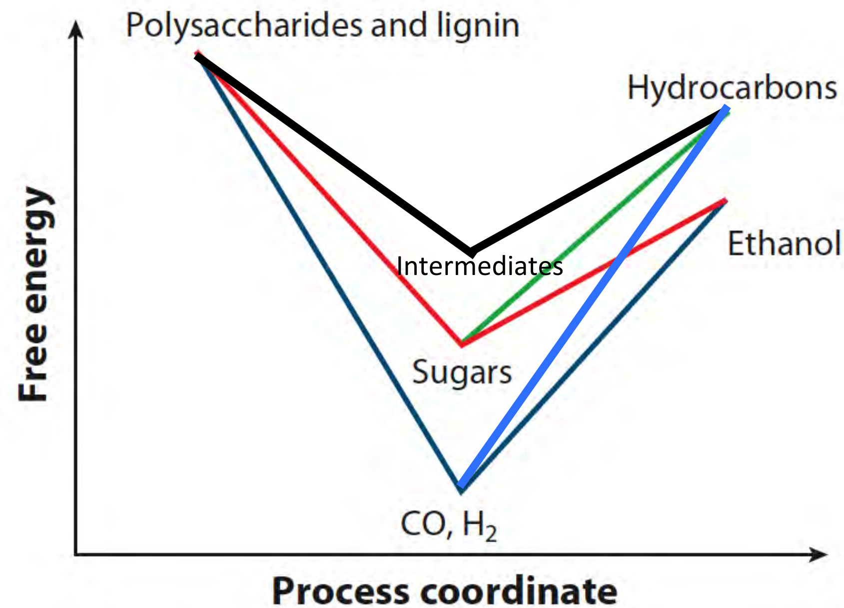


# Gasification

- Technology fairly well developed
- Classes of gasifiers
  - **Air Blown Gasification** (updraft or downdraft) – low cost and thermally efficient, product gas not well suited for fuel synthesis – high $N_2$ content
  - ***Indirect Gasification*** – good thermal efficiency, syngas not diluted with $N_2$ – product gas relatively high in tars
  - **Direct Gasification** – Good product gas, lower in tars, - high cost of $O_2$,, lower thermal efficiency, syngas high in $CO_2$
  - **Entrained Flow Gasification** – Excellent product gas, essentially no tars – high cost of $O_2$, low thermal efficiency, higher capital cost because of increased complexity

# Thermodynamics and kinetics of biomass conversion

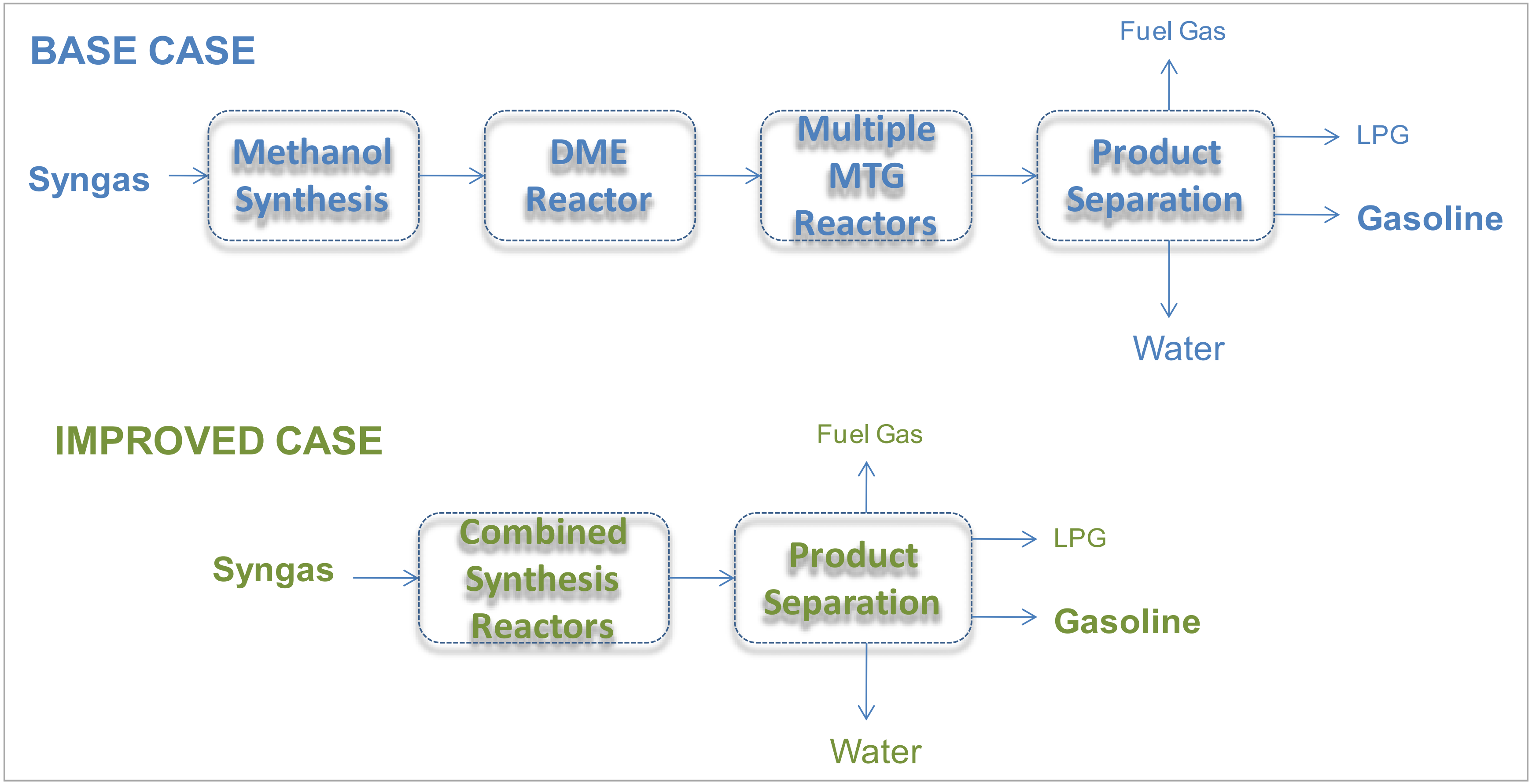



- Gasification is inherently a lower efficiency process based on thermodynamic analysis

# Challenge - Fuel Synthesis is Process/Capital Intensive

Need to simplify the process to achieve economics



# Pros/Cons and challenges of gasification routes

**Pros**

- Good experience base
- Only significant technical challenge is cost and complexity
- Capable of producing high quality diesel and jet fuels
- Chemistry works and is relatively proven

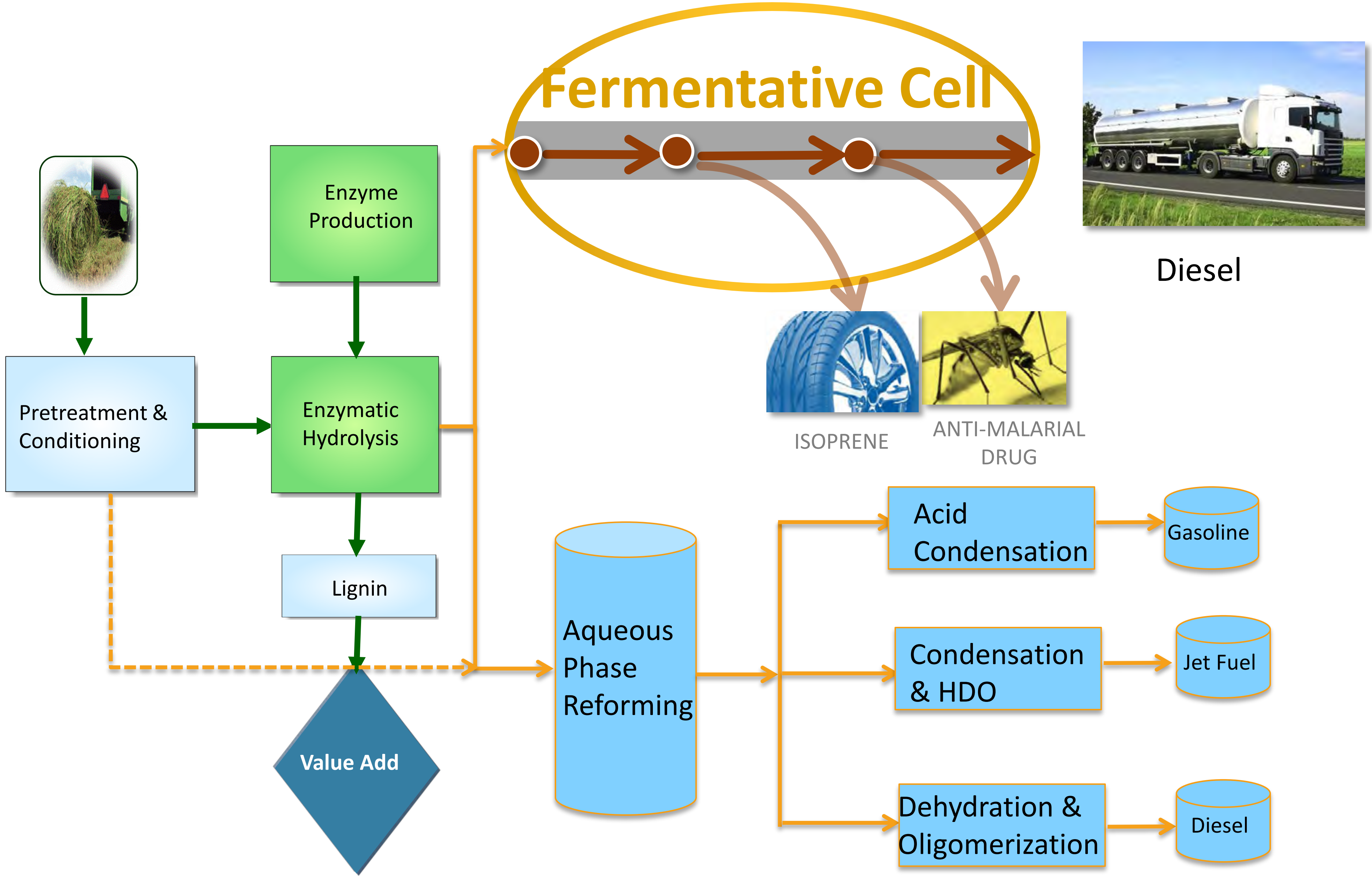
**Cons**

- Cost is a significant challenge
  - Previous attempts to reduce costs have met with limited success

**Challenges**

- Reducing capital costs
- High process complexity

# Sugar or Soluble Carbon Intermediate Pathway

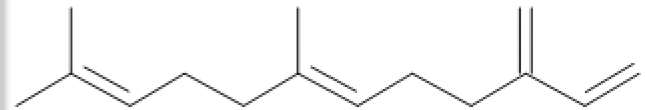


# Fermentation Pathway

hydrolysate

**YEAST CELL**

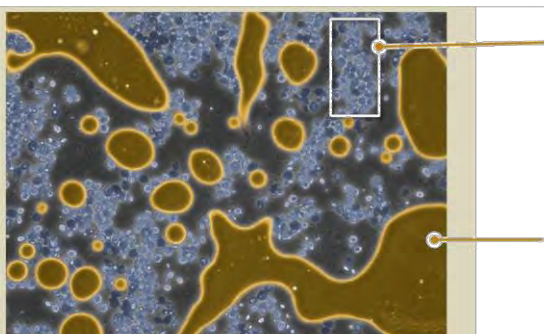
Mevalonate Pathway



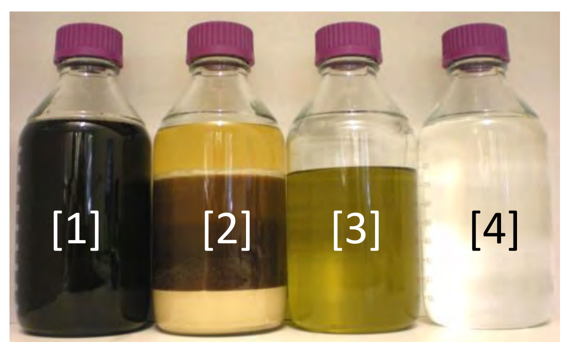
β-Farnesene

**Farnesene Synthase**

Diesel & Chemical Precursor

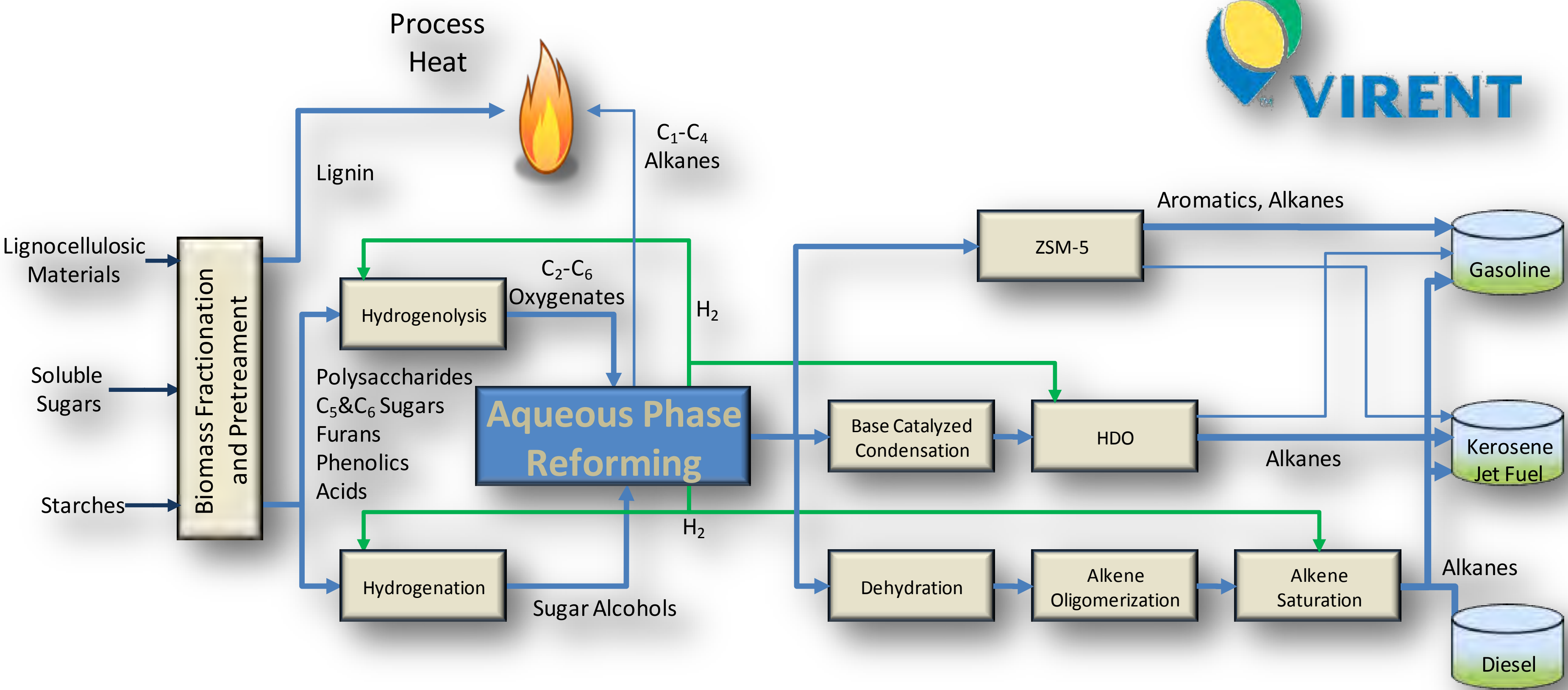



Phase-Contrast Micrograph of Amyris Engineered Microbes Producing Farnesene



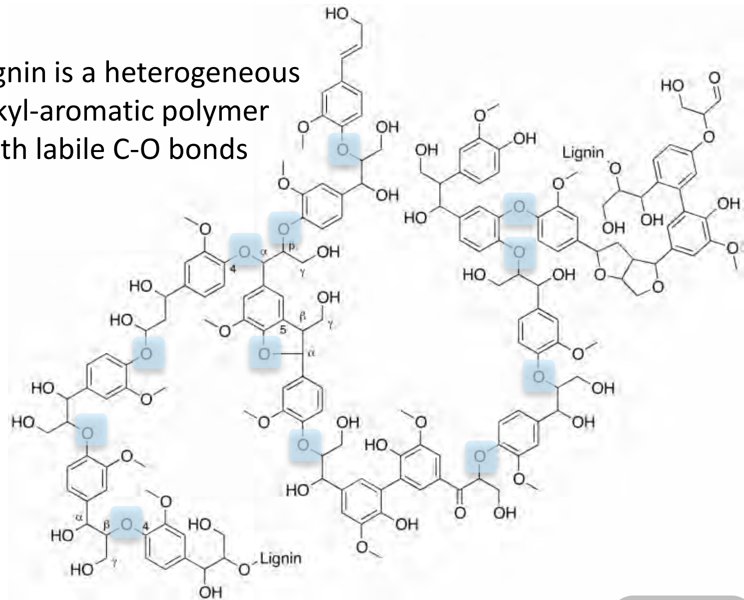

[1] Cane juice
[2] Fermentation broth
[3] Separations
[4] Purification

# Catalytic Pathway



# Extracting from lignin via low energy approaches

Lignin is a heterogeneous alkyl-aromatic polymer with labile C-O bonds

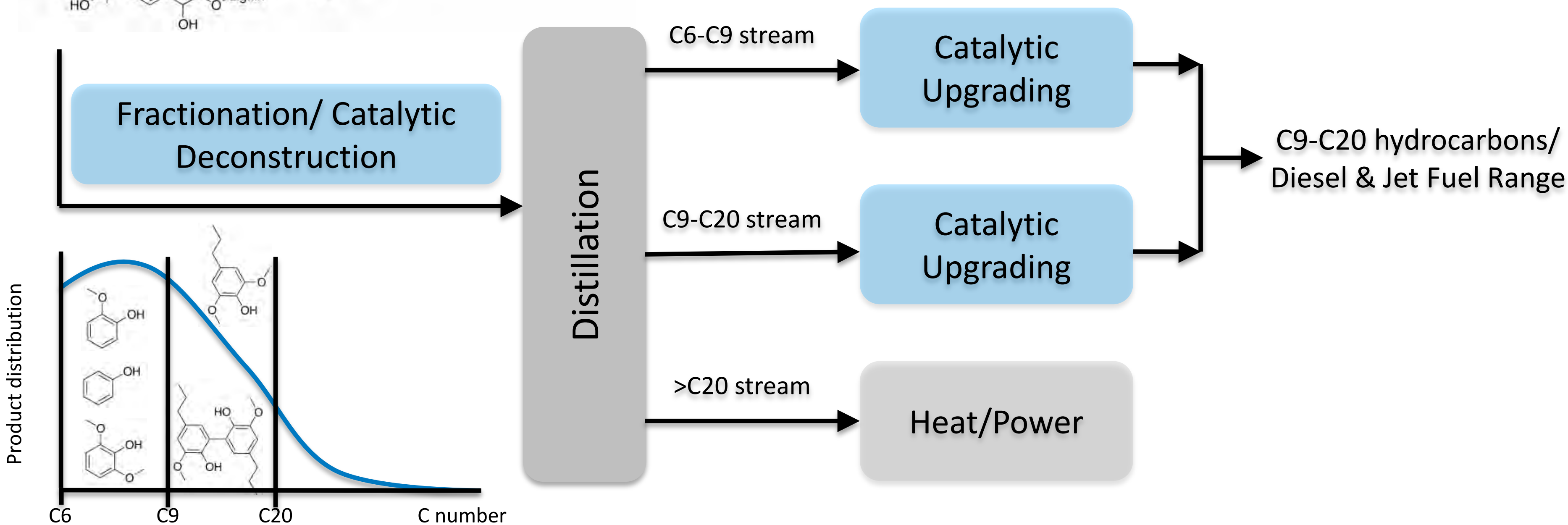



Research needs:

- Fractionation process development
- Catalyst and process development for lignin deconstruction
- Catalyst and process development for lignin upgrading to fuels

Potential strategies

- Fractionation: lignin post Prt/EH, upstream fractionation of carbs/lignin
- Deconstruction: base-catalyzed depolymerization, acid hydrolysis, transition metal catalysts
- Upgrading: Retro-Diels Alder, partial ring saturation, selective ring opening, acid oligomerization



# Pros/Cons and challenges of sugar routes

**Pros**

- Produces high quality components for diesel and jet – both fermentative and catalytic routes
  - Initial higher value applications
- Builds upon OBP cellulosic ethanol technologies so good building base

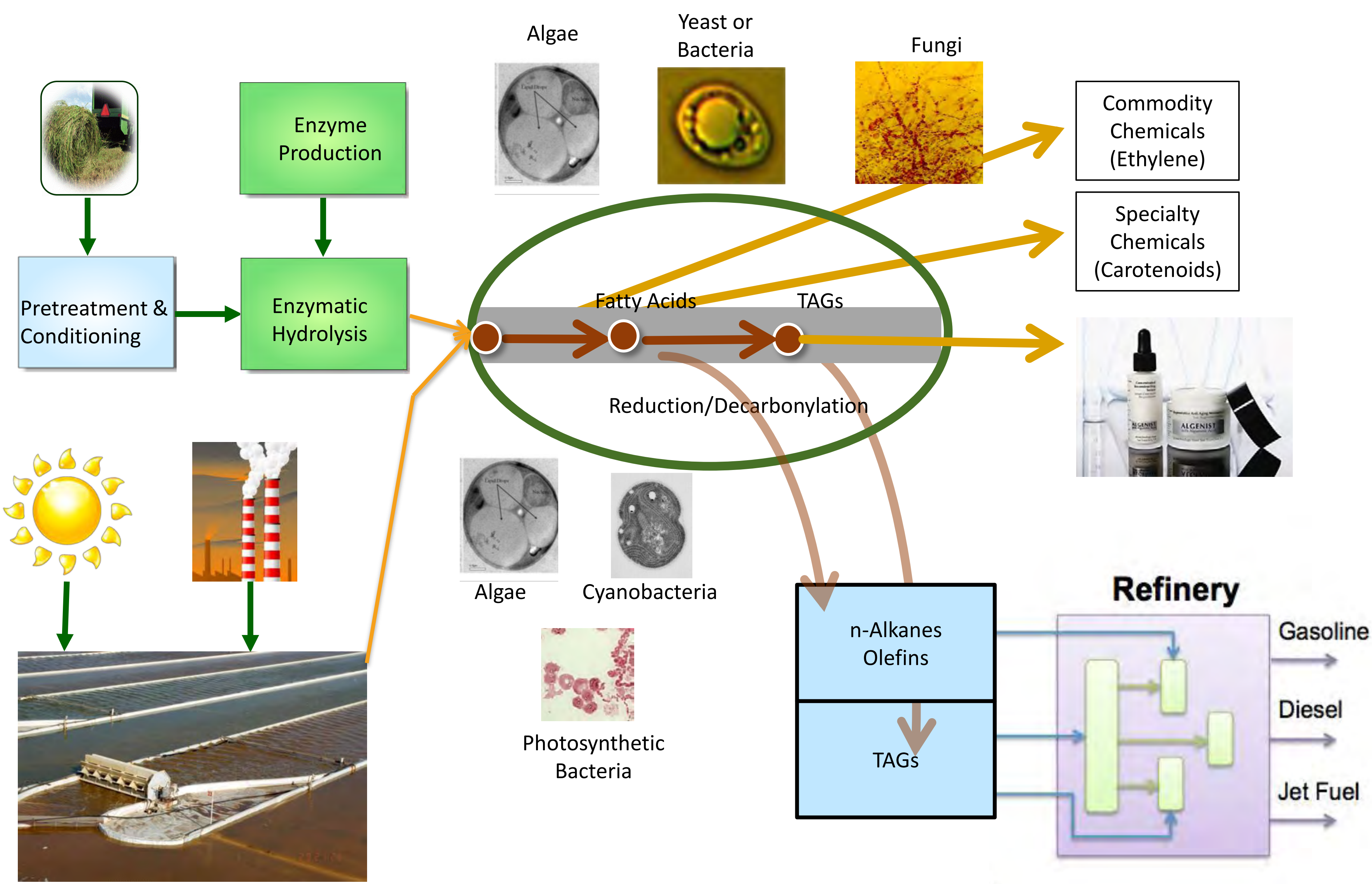
**Cons**

- High capital cost approaches
- Overall yields and efficiencies lower than thermal routes
- Lignin component only used for heat and power at high capital cost

**Challenges**

- Better organisms –fermentative
- Better catalysts – catalytic
- Lower costs
- Better utilization of lignin

# Lipid (Autotrophic/Heterotrophic) Intermediate



# Algal routes to advanced biofuels

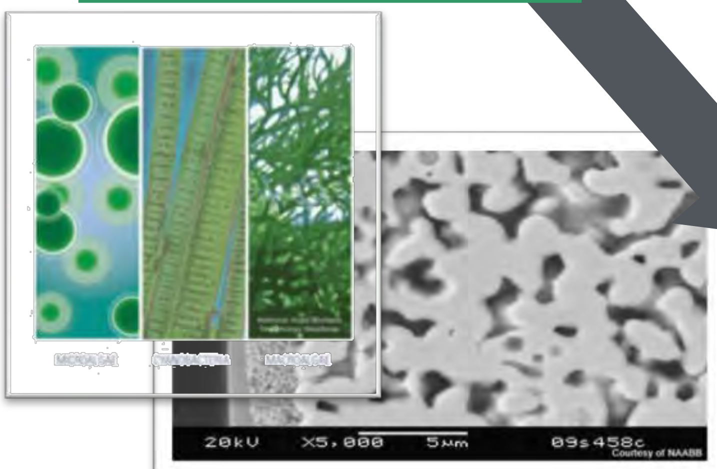
National Alliance For Advanced Biofuels and Bio-products

## Biology and Cultivation


- Algal Strains - Growth, productivity, stability, and resilience
- Cultivation system design
- Temperature control
- Invasion and fouling
- Input requirements
- $CO_2$, $H_2O$ sources, energy
- Nitrogen and phosphorous
- Siting and resources

## Biomass Harvesting and Recovery

- Energy efficient harvesting and dewatering systems
- Biomass extraction and fractionation
- Product purification




A nano-membrane filter being developed by a NAABB partner.

## Conversion and End-use

A gasifier being used by a NAABB partner to convert algal biomass to fuels

- Process optimization
  - Thermochemical
  - Biochemical
- Fuels characteristics
- Co-Products

# Pros/Cons and challenges of algal routes

**Pros**

- Capable of producing high quality fuels
- High yields
- Negates food versus fuel debate
- Does not need fresh water

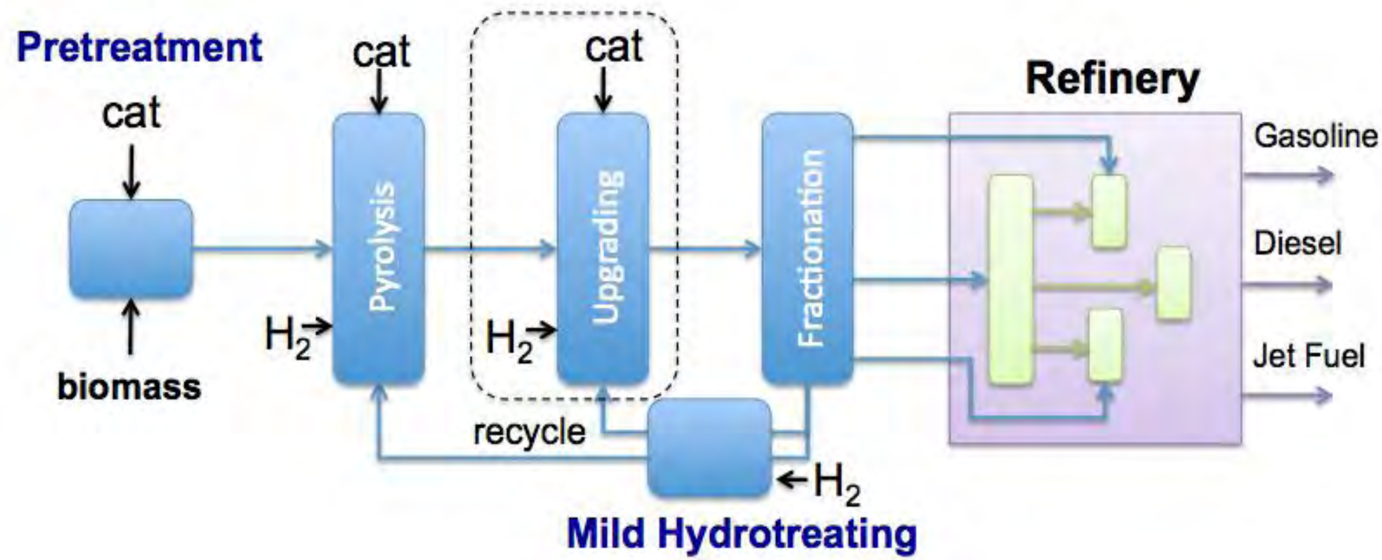
**Cons**

- Significant technical risk
- Cost barriers significant and numerous

**Challenges**

- Cell biology
- Cultivation
- Harvesting and extracting
- Economic uses of cell mass

# Bio-Oil Intermediate




Initial Results (NABC data)

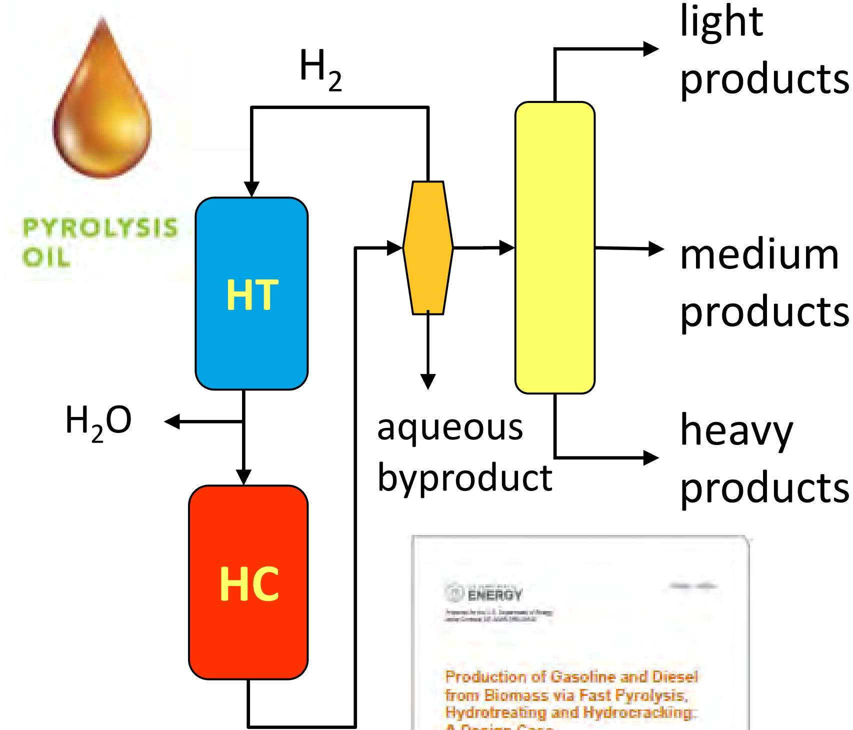
**Good**

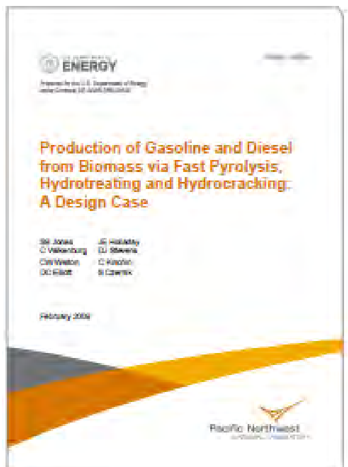
- Feasibility tests very positive
- Economics show the potential to be very attractive (< $2.00 gge for refinery integration case)
- Refiners are very interested

**Bad**

- Products are almost exclusively aromatics mostly in the gasoline range
- Chemistry is very complex and poorly understood making process design dubious

# Fast pyrolysis oil is converted to fuels in a 2-step process





ENERGY

Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case

Pacific Northwest

| Hydroprocessed Bio-oil (from Mixed Wood) | | | Petroleum Gasoline |
|---|---|---|---|
| | Min | Max | Typical |
| Paraffin, wt% | 5.2 | 9.5 | 44.2 |
| Iso-Paraffin, wt% | 16.7 | 24.9 | |
| Olefin, wt% | 0.6 | 0.9 | 4.1 |
| Naphthene, wt% | 39.6 | 55.0 | 6.9 |
| Aromatic, wt% | 9.9 | 34.6 | 37.7 |
| Oxygenate, wt% | | 0.8 | |

The product carbon recovery based on biomass was about 35%

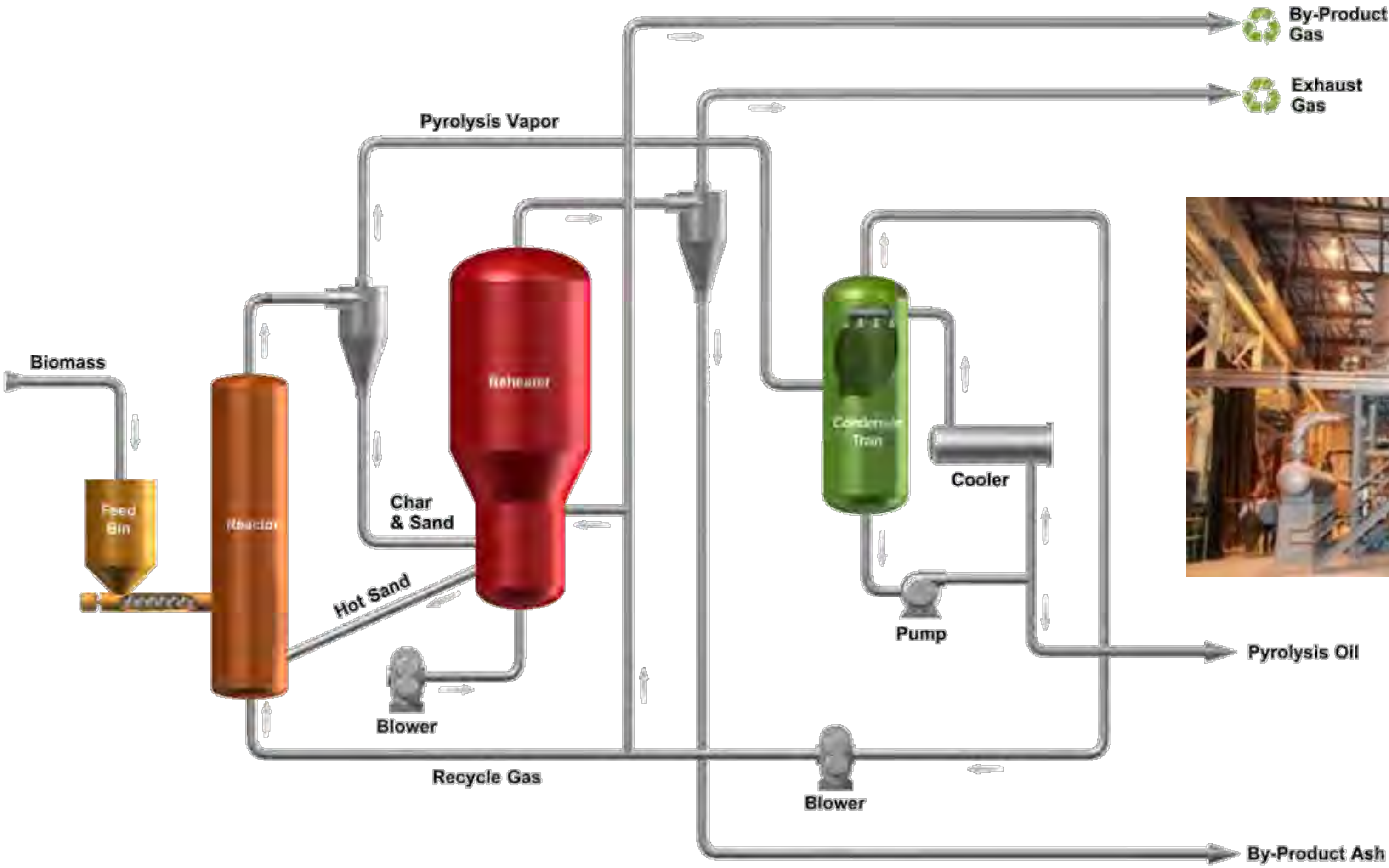
Process is capital intensive

Logistics issue since pyrolysis oil is highly corrosive and unstable

Process may not be scalable or replicable for large volume fuel production without new infrastructure

Holmgren, J. et al. NPRA national meeting, San Diego, March 2008.

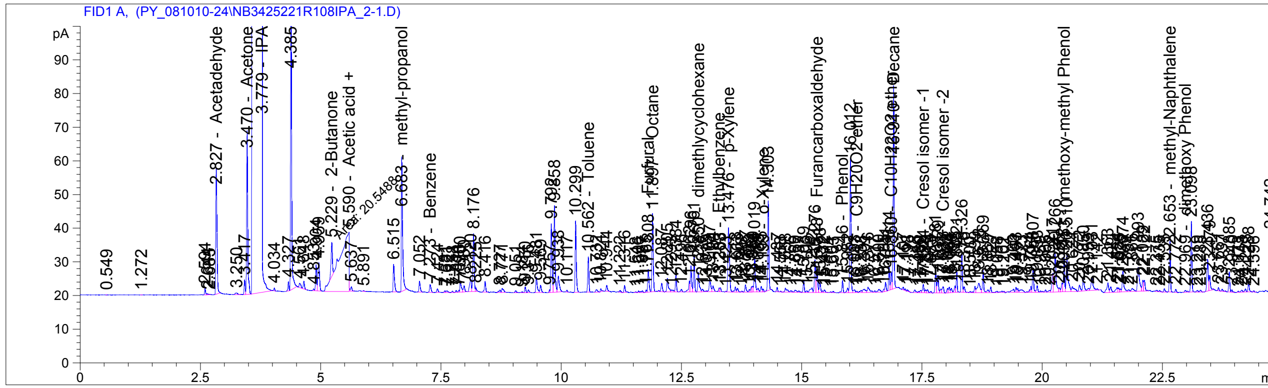
# Catalytic Fast Pyrolysis (CFP) Hydropyrolysis (HYP)



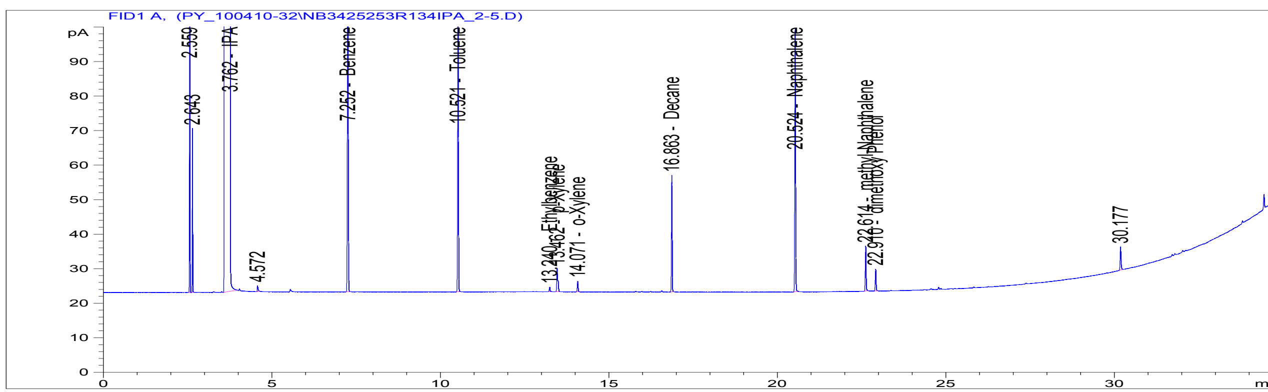

**Based on Fluidized Catalytic Cracking (FCC) Technology Pervasive in Petroleum Refining**

# CFP/HYP Catalyst Impact

## Standard Fast Pyrolysis



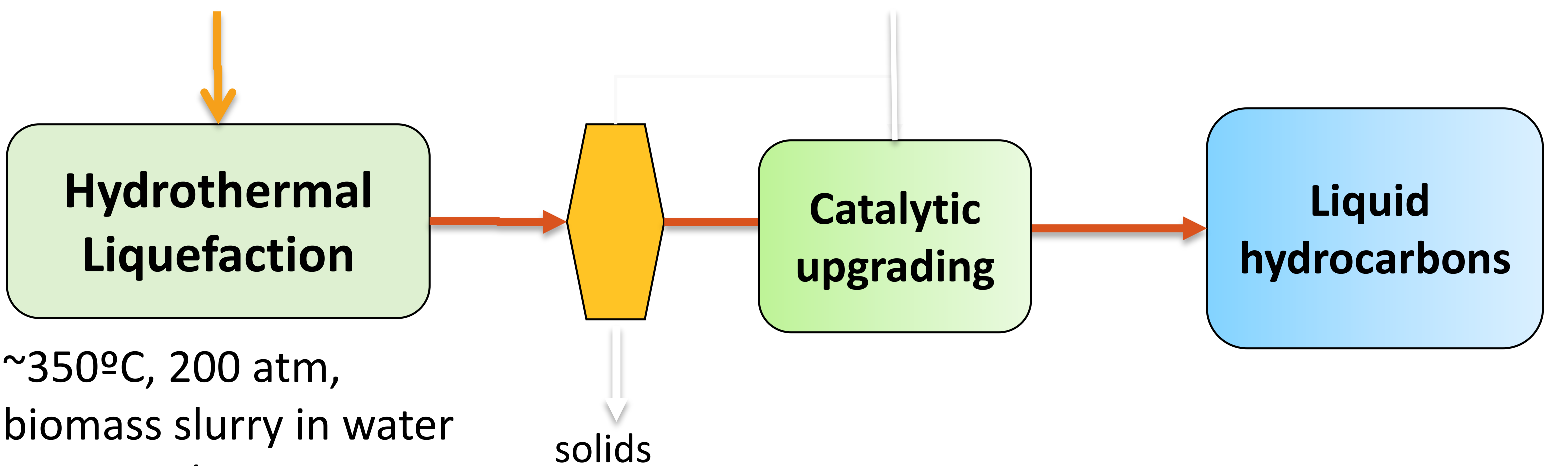

## Catalytic Fast Pyrolysis/Hydropyrolysis




Quality ↑↑ Yields ↓↓

# Hydrothermal Liquefaction

Slow pyrolysis in pH-moderated, pressurized water

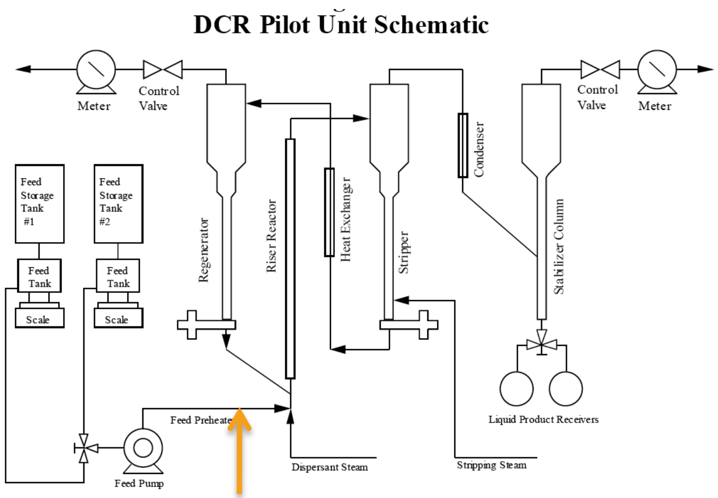



~350ºC, 200 atm,
biomass slurry in water
Long residence times

Biomass slurry feed (15% solid)

HTL Oil Product (at 25 °C)

# Bio-Oil Intermediate Research Needs




Pyrolysis Vapor
4" FBR

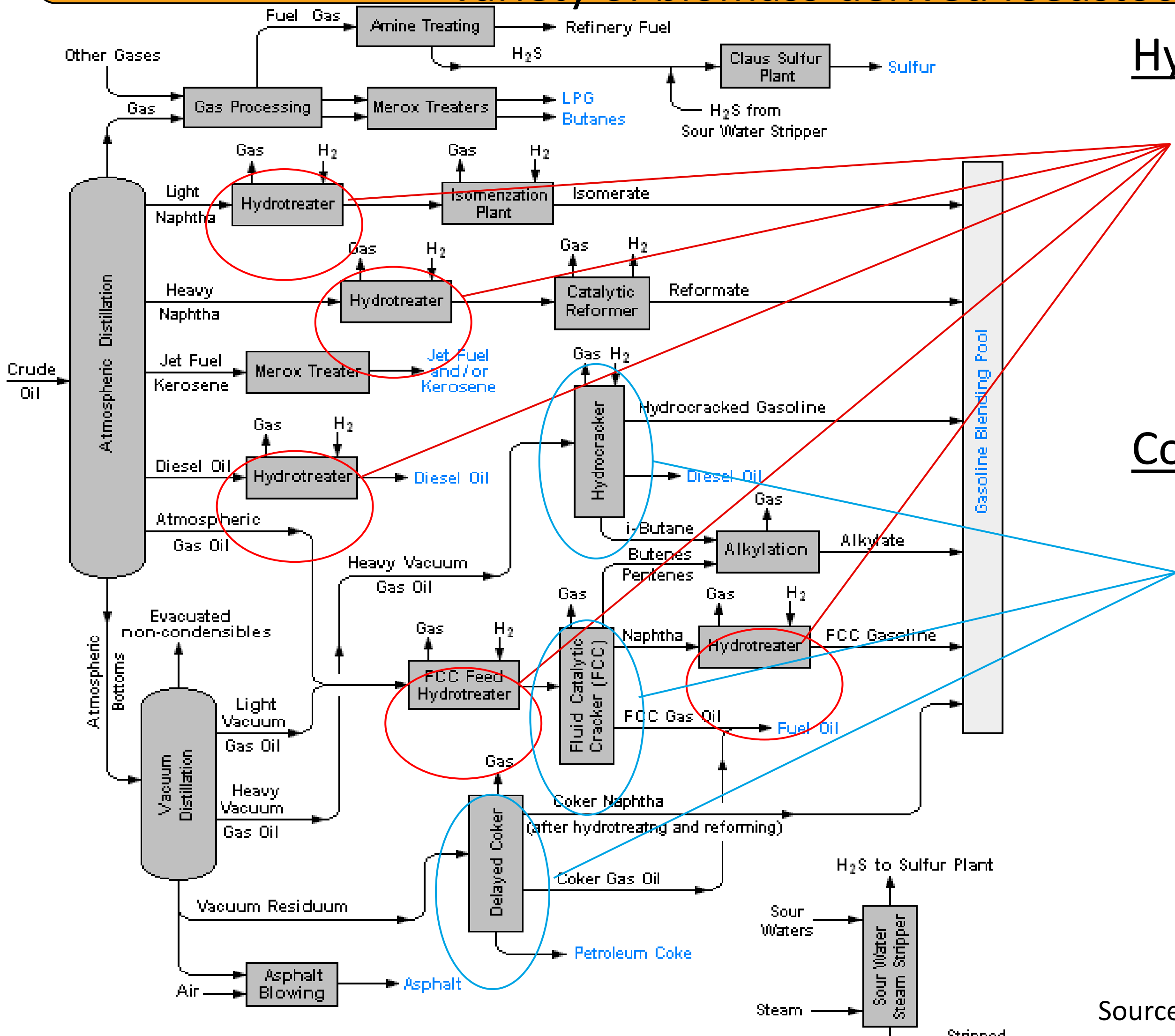
**Research Needs**

- Determine chemistry mechanisms
  - Minimize BTX (aromatics)
  - Form C-C bonds towards diesel and jet fuels (straight and branched chain alkanes)
- Develop and test deoxygenation catalysts
- Test catalyst deactivation and regeneration
- Produce sufficient quantities of oil for refinery integration testing
- Investigate effects of catalytic pyrolysis (effects of alkali metals, etc)
- Test in reactor representative of petroleum refinery FCC reactor

This area has very big promise but significant research needs to be done

# Potential Co-Processing Points

Refineries contain many potential insertion points for co-processing of a variety of biomass-derived feedstocks




## Hydroprocessing Units

- Typically designed to remove sulfur
- Potentially suitable to deoxygenate triglycerides or other bio-oils

## Conversion Units

- Designed to break down larger molecules into smaller ones
- Potentially suitable for upgrading of pyrolysis oils into fuels

Source: Wikipedia

# Conclusions

- **Ethanol future still uncertain**
  - Café standards driving to higher compression engines
  - Significant activity in commercialization
  - Butanol also a possibility
- **Future is advanced biofuels "drop- in". Although preliminary results are promising many challenges remain:**

  **Biomass**
    - Yields and costs
    - Lignin utilization
    - Must integrate into future fuel mix need

  **Algae**
    - Significant technical challenges
      - Cell biology
      - Cultivation
      - Harvesting
      - Cell mass utilization

# Biomass for Transportation Deployment

| | Near Term Impact (< 5 yrs) | Mid Term Impact ( 5-10 yrs) | Long Term Impact (> 10 yrs) |
|---|---|---|---|
| **Biofuels Deployment** | **Biochem/Thermochem Cellulosic Ethanol**<br>**Advanced Biofuels From Simple Sugar Feedstocks** | **Advanced Biofuels Lignocellulosic Feedstocks**<br>- Gasoline<br>- Diesel<br>- Jet Fuel<br>**Algal Biofuels R&D**<br>- Gasoline<br>-Diesel<br>-Jet | **$4^{th}$ Gen Biofuels**<br>- direct photosynthesis<br>-GMO plants |
| **Biopower** | Cofiring | IGCC | Battery Electric Vehicles |
| **Analysis** | **Pathway Technoeconomic Analyses**<br>**Sustainability Analysis**<br>- Cellulosic ethanol<br>- Advanced biofuels | **Advanced Biofuels Market Analysis**<br>- $3^{rd}$ generation<br>- $4^{th}$ generation | **Breakthrough Technology Anal.**<br>- direct PS<br>-Genetically modified plants |


# Questions?

***Biomass for Advancing America***

# Pros/Cons and challenges of catalytic pyrolysis routes

**Pros**

- Based on proven technology – FCC technology in petroleum industry
- Low cost – both operating and capital
- Integrates well with petroleum refining

**Cons**

- Produces only gasoline and only aromatics which are least desirable from a refinery perspective
- Produces a less desirable co-product steam that must be utilized to achieve economics and GHG benefits

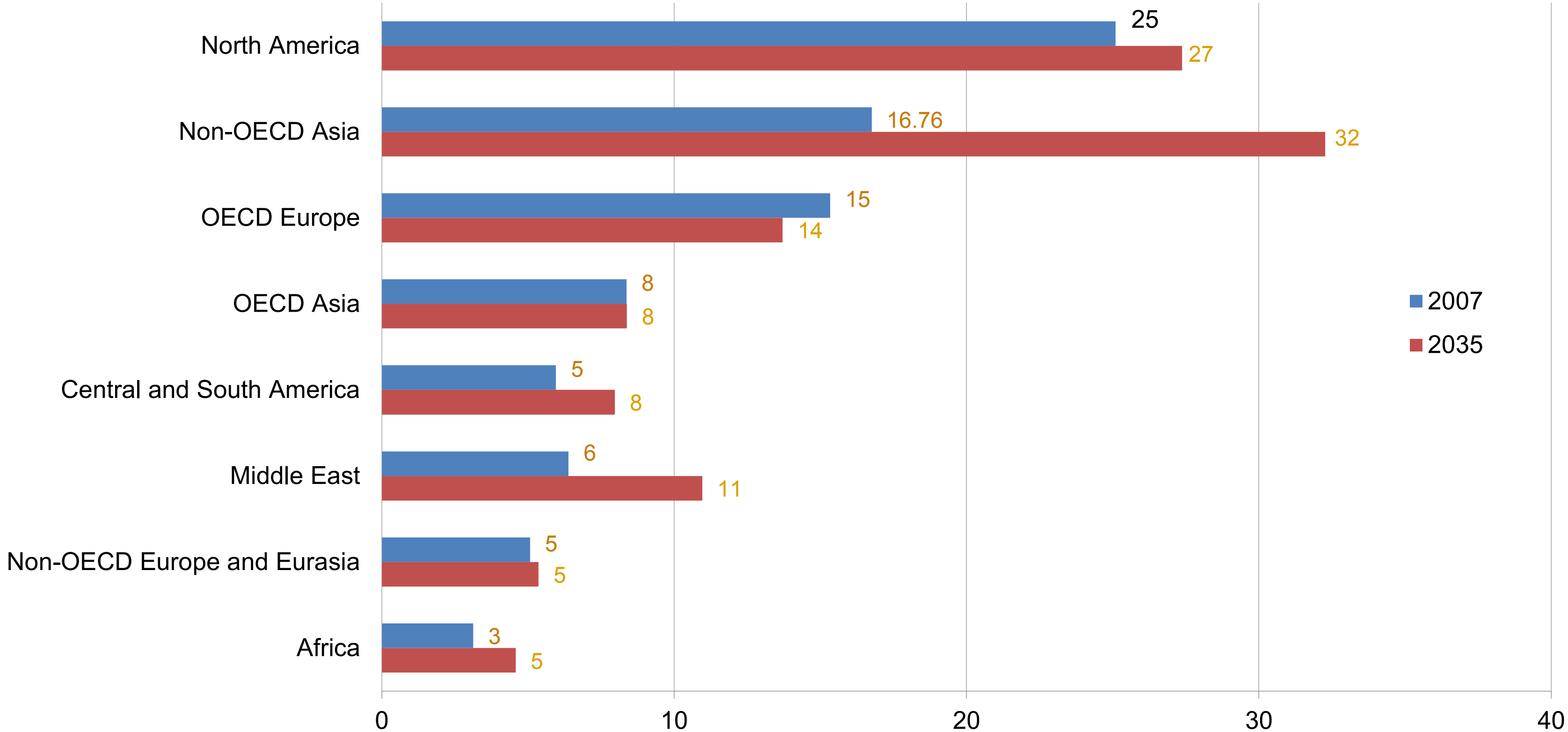
**Challenges**

- Better catalysts
- Shift product ratio to higher percentage of fuel  fraction versus co-product portion
- Better understanding of underlying chemistry

# U.S. demand is leveling off but world wide demand is rapidly increasing

**Figure 27. World liquids consumption by region and country group, 2007 and 2035**

million barrels per day



# US Situation – future looking better

Figure 11. Total energy production and consumption, 1980-2035
(quadrillion Btu)

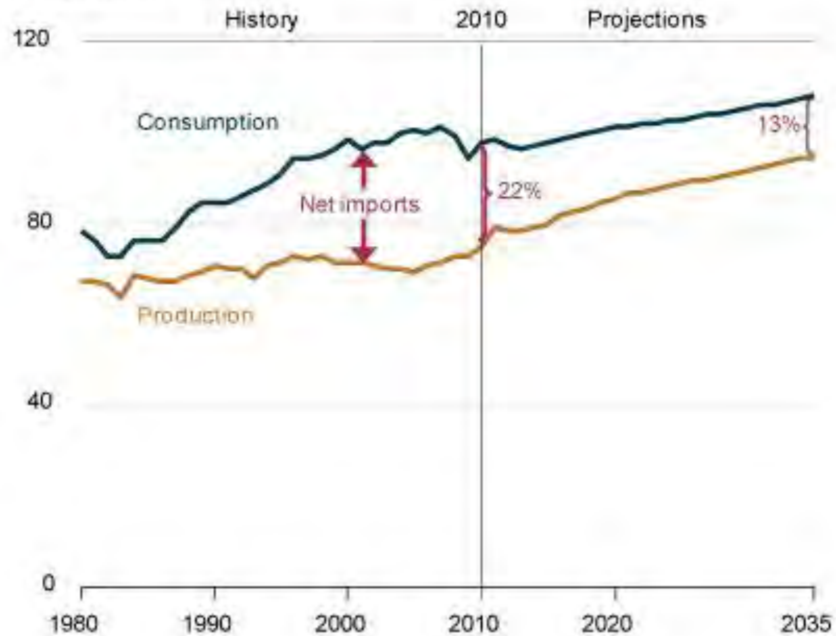
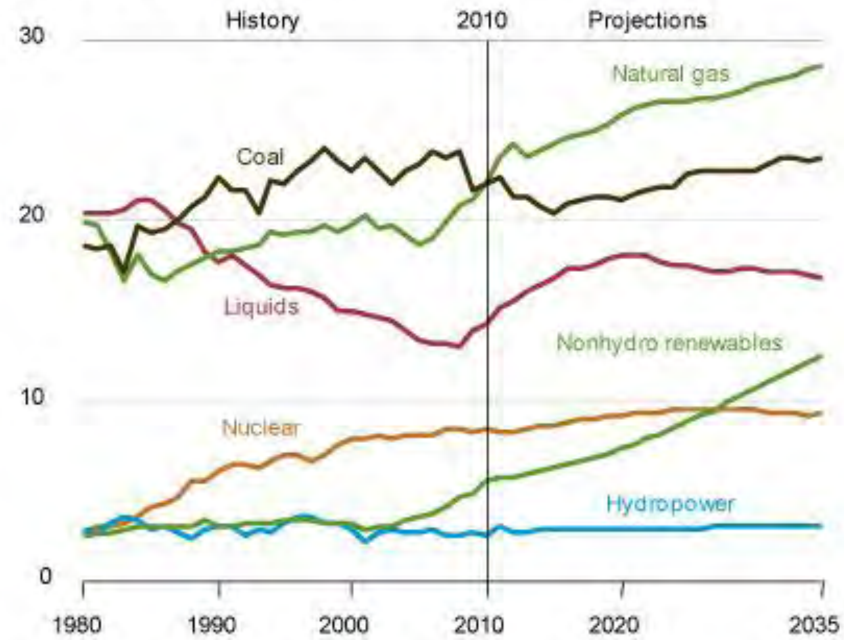



Figure 12. Energy production by fuel, 1980-2035
(quadrillion Btu)



# But…. Nobody likes

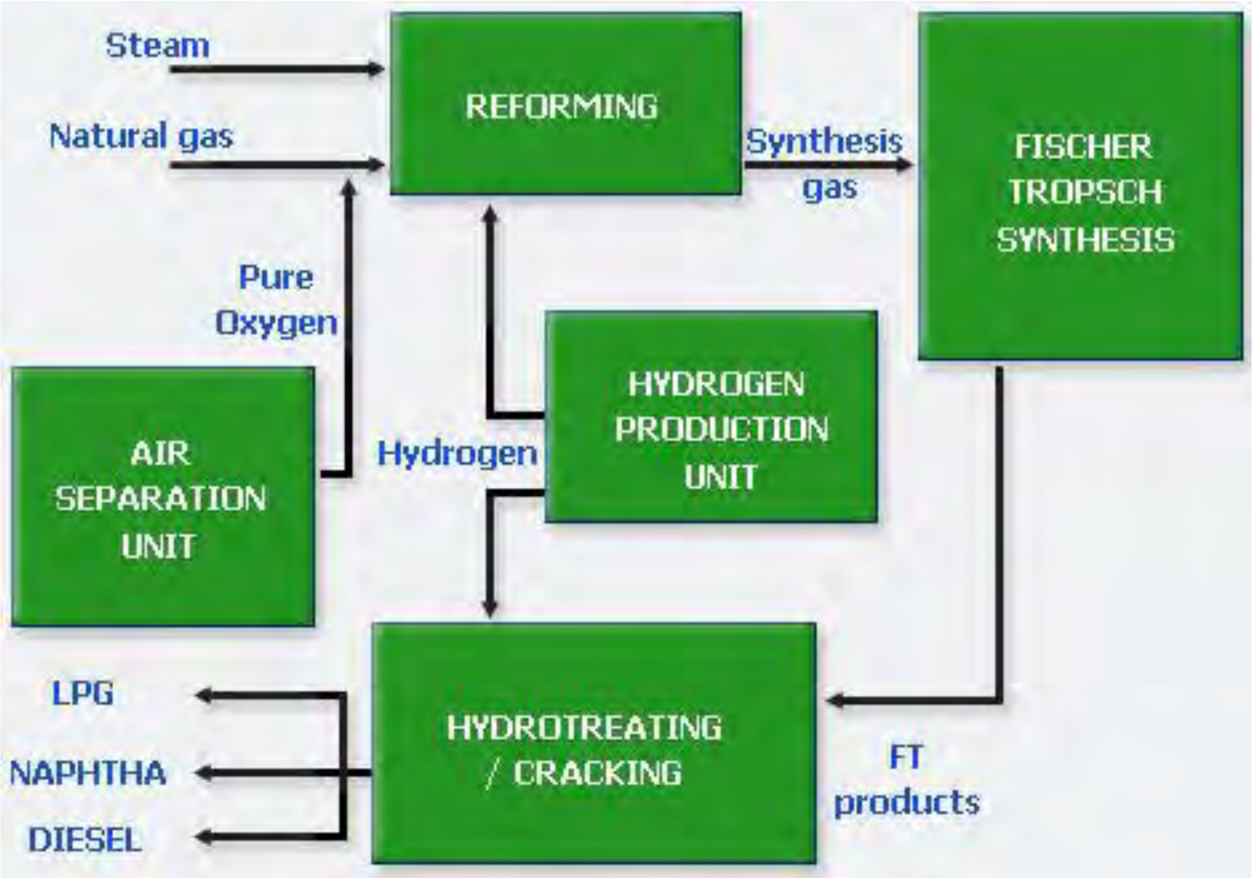
- CNG vehicles – short range, safety issues in a crash and trunk taken up by large tanks
- Ethanol – lower mileage, higher food prices plus specialty engine issues
- Small underpowered cars and hybrids

# Need

- Better fuel efficient vehicle options
- Better natural gas vehicles and/or better fuels from natural gas – gas to liquids
- Better biofuels

# Natural Gas to Liquid Fuels (Gasoline (naptha), Diesel and Jet Fuel)

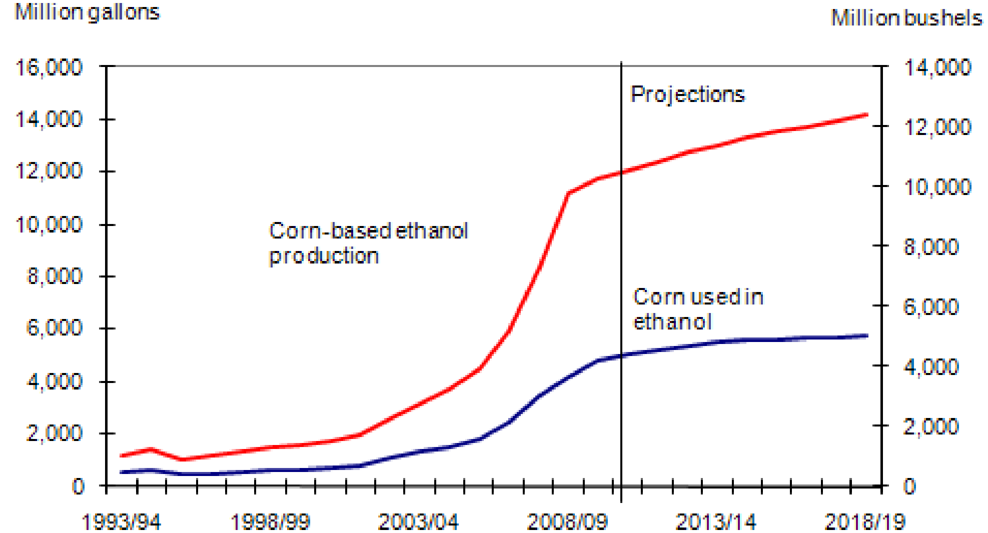
Fischer-Tropsch Process



# Corn Ethanol

- 97% of gasoline used in U.S. is E10
- 14 Billion gallons produced in 2011
- 40% of US corn crop is used for ethanol production
- Ethanol production is the biggest use of corn has now overtaken animal feeding
- Much debate on the impact on food prices but corn prices have doubled over the past decade from historic levels
- No detrimental impact on modern cars (2000 and newer) however can have negative impacts on lean burn, marine or small engines

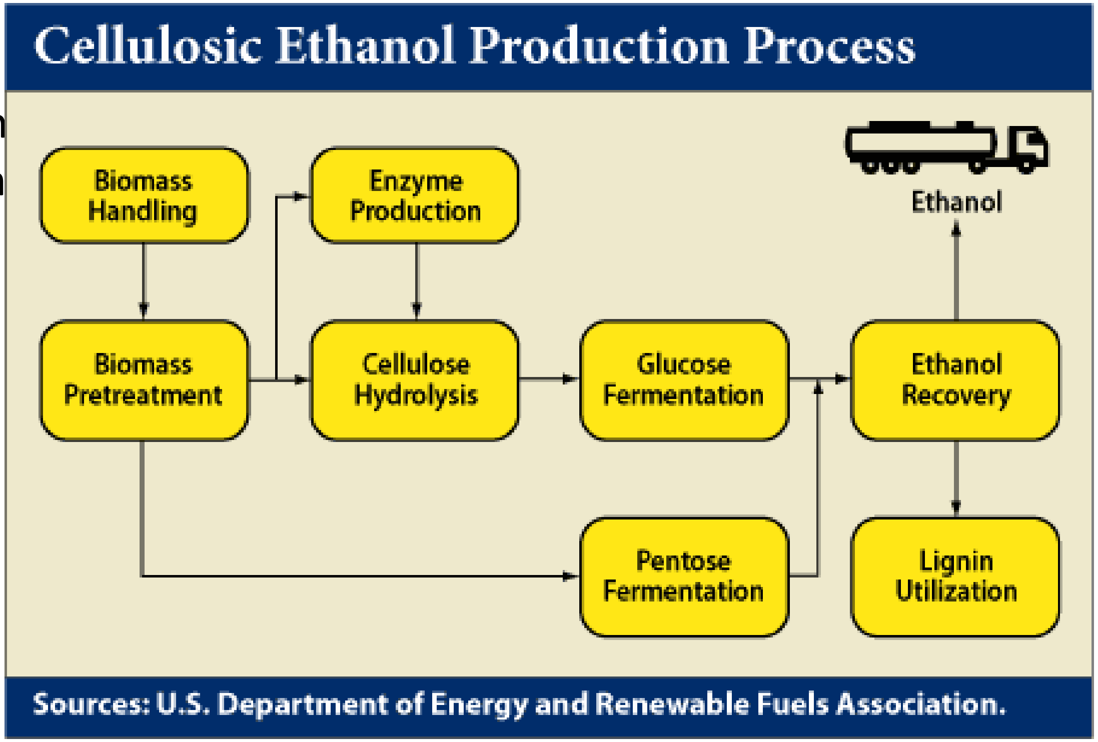
**Million gallons of corn based ethanol production and million bushels of corn used in ethanol production**



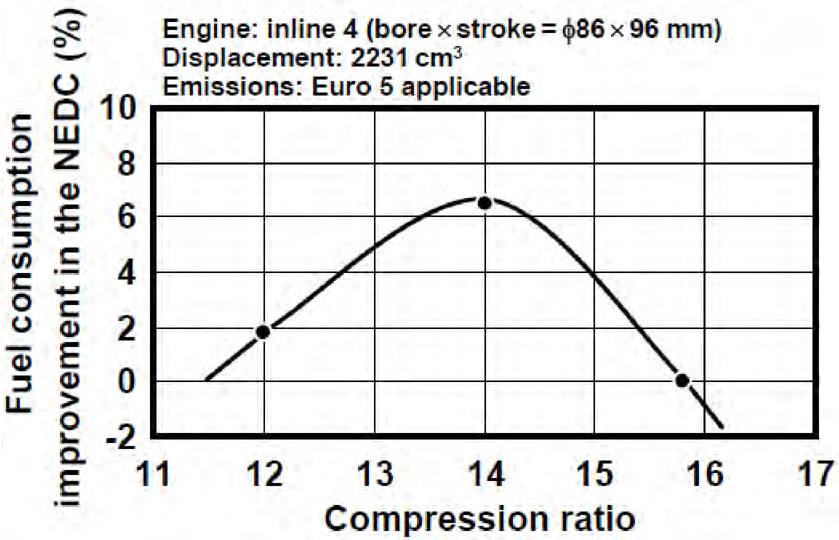

Source: *USDA Agricultural Projections to 2019*, February 2010. USDA, Economic Research Service.

# Cellulosic Ethanol

- Made from plant material not corn and hence does not compete with food
- Environmentalists like it better – lower $CO_2$ emissions and environmental impacts in general
- Higher cost near-term, lower-cost long-term
- Still ethanol

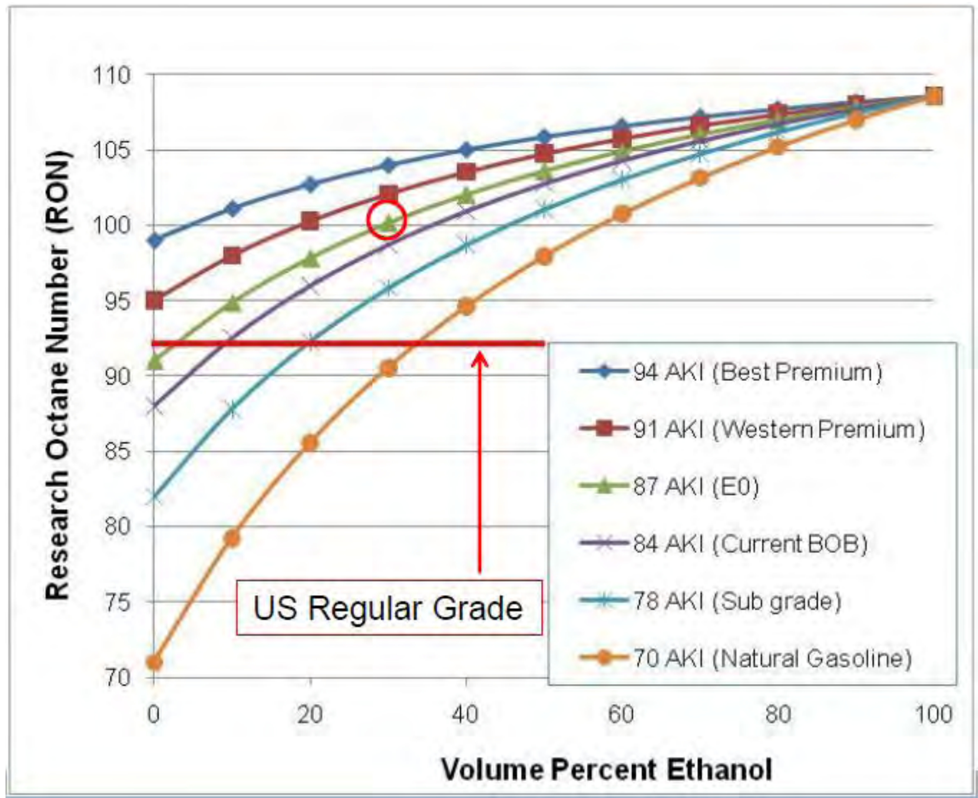


# Ethanol Can Enable More Efficient Engines




- Higher compression ratio yields higher efficiency
- Above CR of 14 piston ring friction dominates
- CR=14 is optimal
- Current engine CR about 10

- **Higher CR would be enabled by HIGHER Octane Number**
  - Ethanol has a much higher blending Octane Number than hydrocarbon blendstocks
  - Another advantage of ethanol is cooling effect of vaporization – much greater than hydrocarbon



## Why not just make gasoline, diesel and jet from biomass

**Gasoline (cars & trucks)**

**140 bgy**

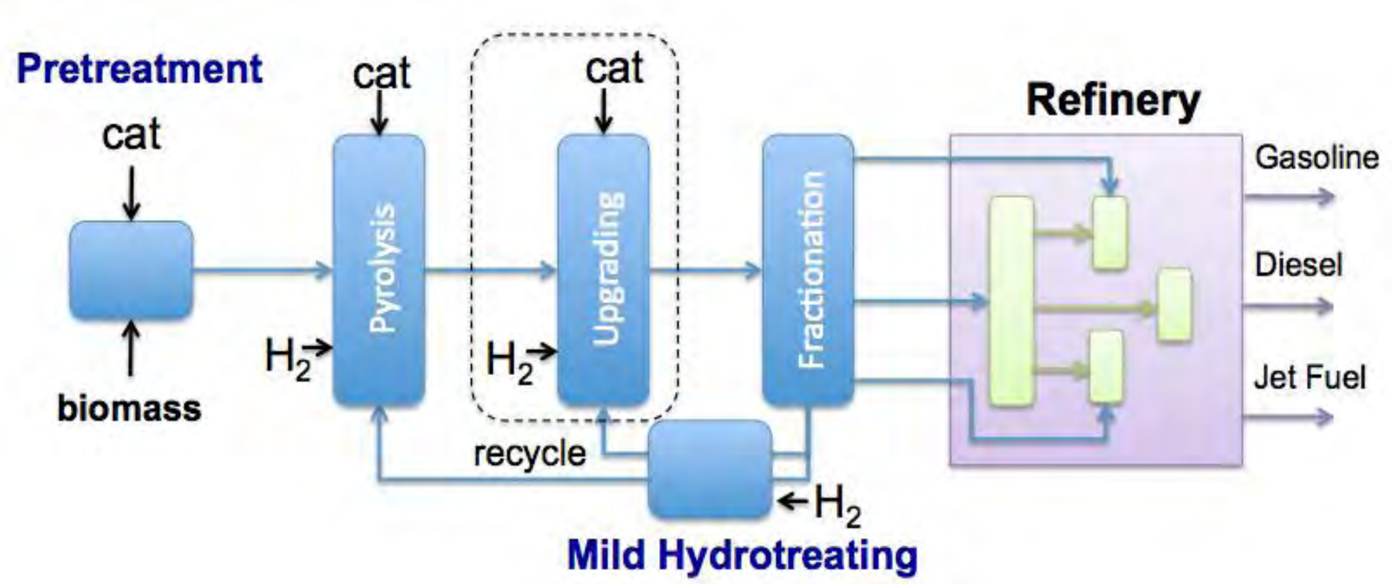
**Diesel (on-road, rail)**

**43 bgy**

**Aviation (jet fuel)**

**25 bgy**

# Make biomass a liquid




Initial Results

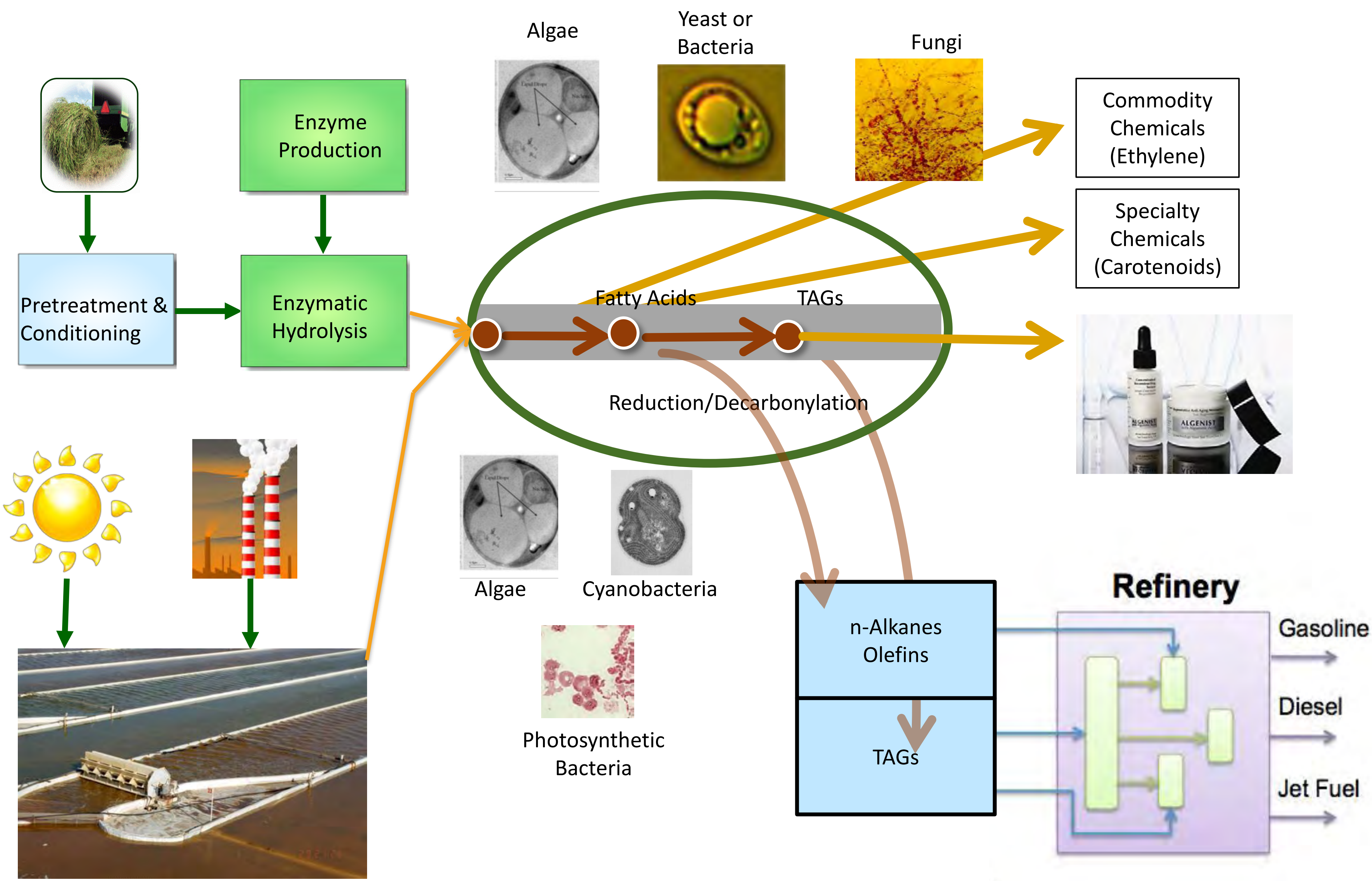
**<u>Good</u>**

- Feasibility tests very positive
- Economics are superb (< $2.00 gge for refinery integration case)
- Refiners are very interested

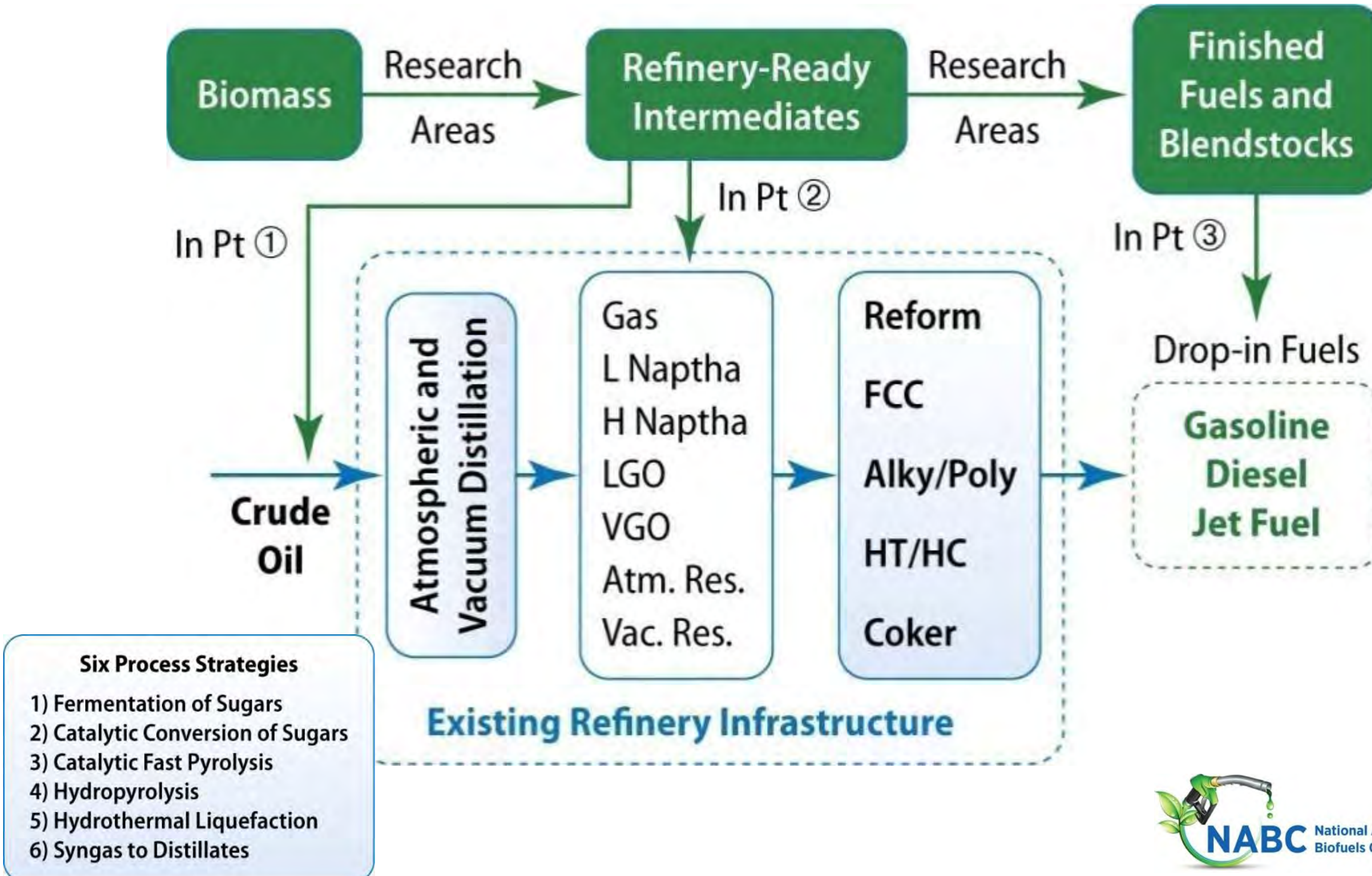
**<u>Bad</u>**

- Products are almost exclusively in the gasoline range
- Chemistry is very complex and poorly understood making process design dubious

# Fuels from Algae



# Co-Process biomass with petroleum




NABC National Advanced Biofuels Consortium

# Evolution of Cars

**1970s Car**

- 15.8 mpg
- 136 hp
- 0-60 in 14.2 seconds
- carbureted
- 3 spd transmission
- Minimal emission controls

**2012 Car**

- 32.7 mpg
- 192 hp
- 0-60 in 9.5 seconds
- Direct injection
- 6 -8 spd transmission
- Emit 95% less pollutants – sophisticated electronic engine management systems

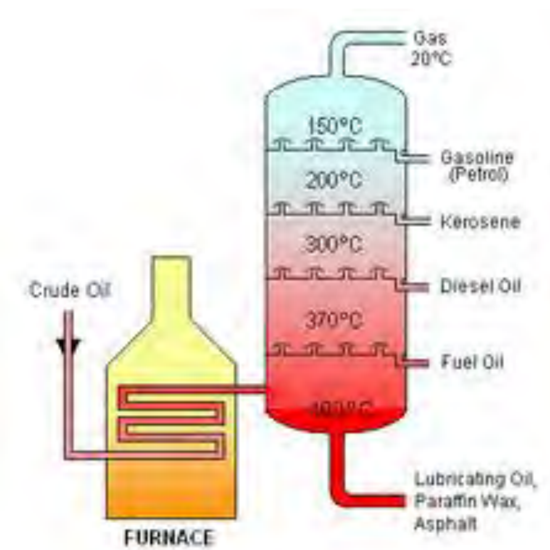
# Evolution of Fuels

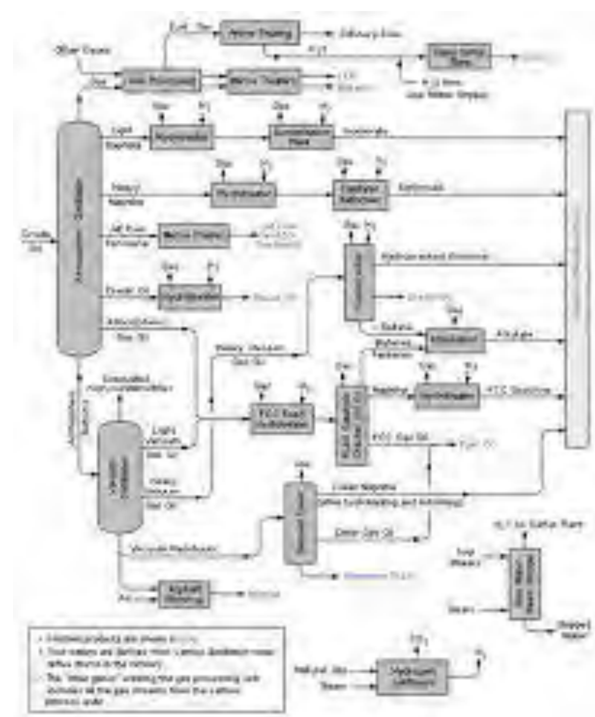
**1970s Refinery**

- **Distillation only**
- **Sulfur 1000 ppm**
- **Minimal specs**
- **No specs on N levels**
- **Leaded to bypass octane ratings**

**2012 Refinery**

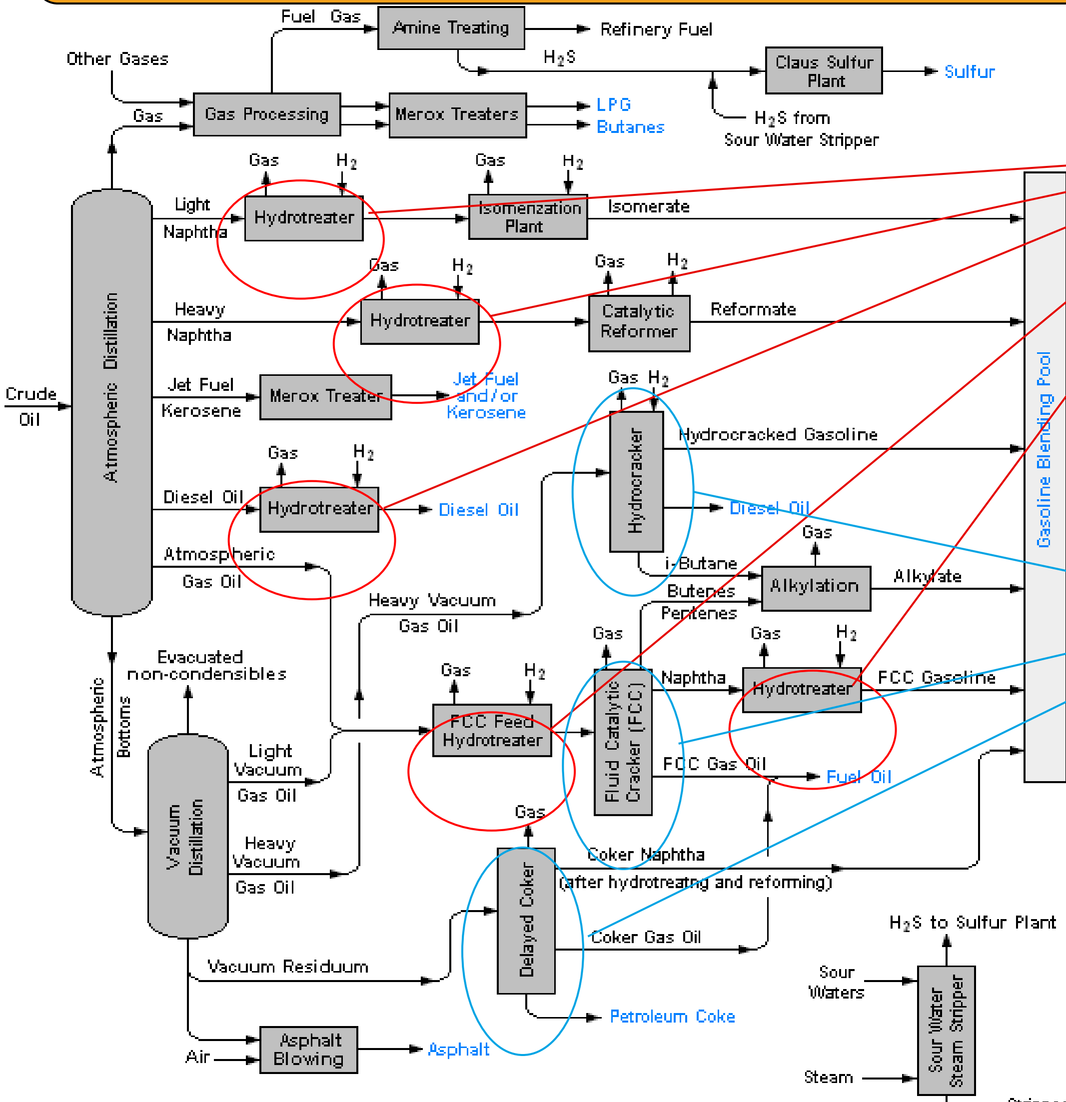
- **Multiple processes**
- **Sulfur < 15 ppm**
- **Must blend ethanol, RFS, CAA**
- **Extensive specifications that vary by region and season**



# Bio-fuels are actually beneficial to making better fuels

Refineries contain many potential insertion points for co-processing of a variety of biomass-derived feedstocks




## Hydroprocessing Units

- Typically designed to remove sulfur
- Potentially suitable to deoxygenate triglycerides or other bio-oils

## Conversion Units

- Designed to break down larger molecules into smaller ones
- Potentially suitable for upgrading of pyrolysis oils into fuels

Source: Wikipedia

# Take away points

- **The days of cheap fuels from petroleum are over**
- **The Middle East controls oil prices**
  - Not the President
  - Not Congress
  - Not the oil companies
- **US situation is improving**
  - Reduce demand
    - More  and better fuel efficient cars and trucks
  - Increase supply
    - Offshore drilling in the near term
    - Canadian tar sands
    - Natural gas to liquid fuels
    - Biofuels (gasoline, diesel and jet fuels)
- **Ethanol may reach 15- 25% of gasoline but E85 is essentially dead**