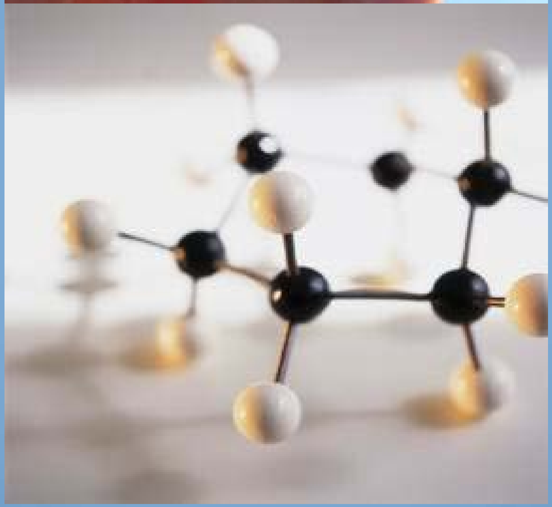


2nd Generation Biofuel Technologies

Paul Grabowski
Office of Biomass Program

January 26, 2011

Strategic Focus for Biofuels

Feedstock Supply → Conversion to Biofuels → Biofuels Distribution → Biofuels End Use



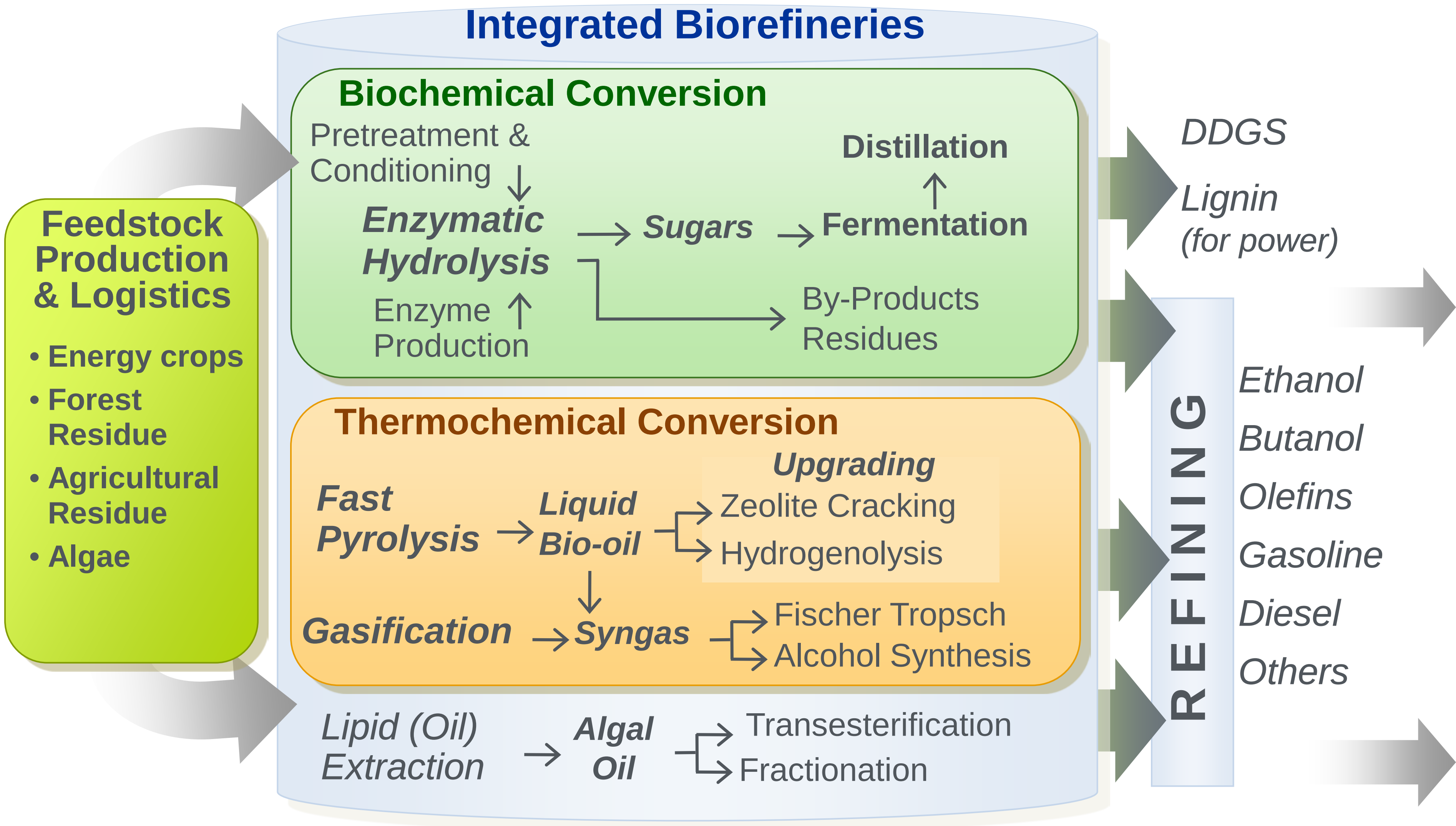


- Expanding and diversifying the portfolio to include renewable hydrocarbon fuels
  - Leveraging bio- and thermo-chemical conversion technology developments from cellulosic ethanol to other advanced biofuels as well as products and power
- Deploying first-of-a-kind facilities and encouraging strong industry partnerships
- Program Targets: (At a modeled cost for mature technology)
  - $1.76/gallon cellulosic ethanol by 2012
  - $2.85/gallon renewable gasoline by 2017
  - $2.84/gallon renewable diesel by 2017
  - $2.76/gallon renewable jet by 2017

Crosscutting Activities

Analysis, Sustainability, Strategic Partnerships, Stakeholder Communications and Outreach

Exploring Routes to Convert Biomass



Research on multiple conversion pathways aims to improve the efficiency and economics of bioenergy production.

First Need – Abundant, Low Cost Feedstock

- Dry Herbaceous – agriculture residues/crops at less than 15% moisture
- Energy Crops – wet, dry, and woody
- Woody – forest resources and woody energy crops
- Strategies to increase feedstock amounts that can be sustainably harvested
- Develop optimal – performing systems integrating feedstock development, production, and conversion components
- Economic assessment of production costs, including logistics
- Feedstock quality designed for optimal conversion efficiency

Thermochemical Conversion – Gasification

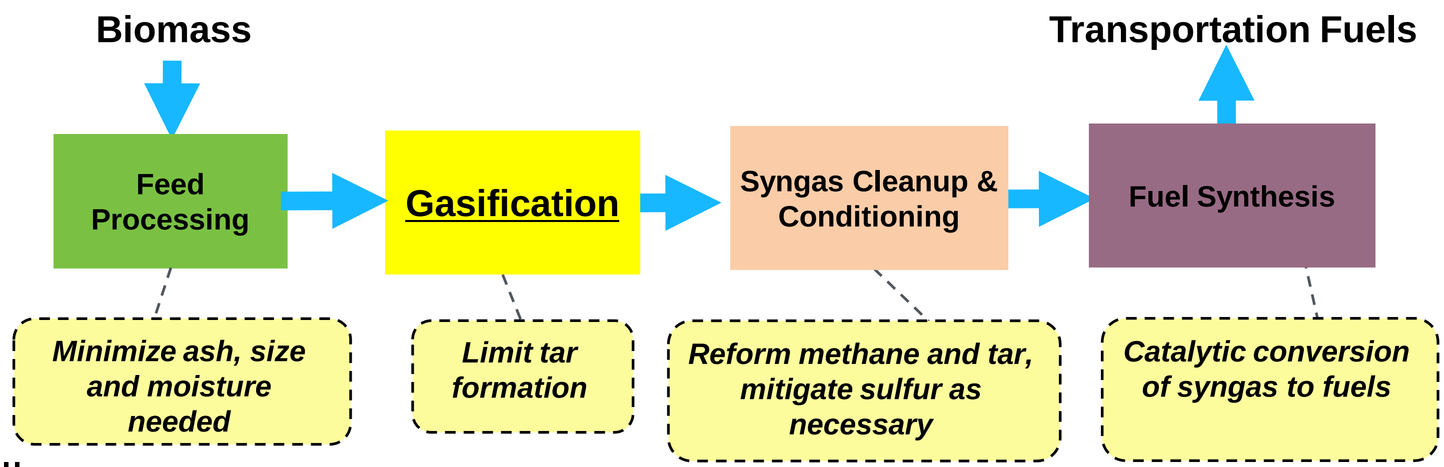
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Current Target

- By 2012, the gasification-to-ethanol process will achieve a conversion cost of $0.86 per gallon of ethanol (2007$s, modeled)

Major Changes

- After 2012 leverage R&D to focus solely on infrastructure compatible fuels

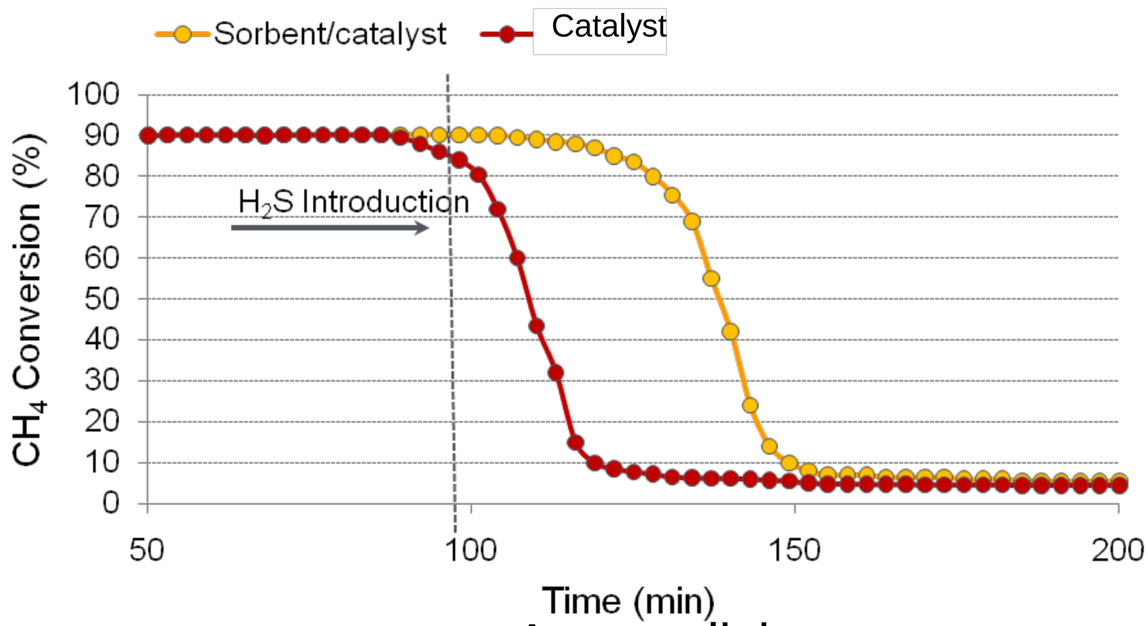


Key Challenges

- Syngas clean up and conditioning
  - (Solicitation: ≤ $7.75 million, Performers: Emery, RTI, GTI, Iowa State University, Southern Research)
- Fuel synthesis
- Operate fully integrated process for > 200 hours

Syngas Cleanup: Contaminant Reduction

Untreated syngas from biomass contains contaminants (S, Cl, P containing gases) that poison tar cracking/methane reforming catalysts.



Rationale

- To remove H_2S, a catalyst poison, at temperature close to gasification and tar reforming temperatures (> 700 °C)
- Inexpensive S sorbents would increase reforming catalyst lifetime

Accomplishments

- Developed a manganese based sorbent that removes H_2S from 1,000 to 1 ppmv in simulated biomass syngas
- Demonstrated with real biomass syngas produced from corn stover

Energy & *Fuels*, 23: 5291□5307 (2009)

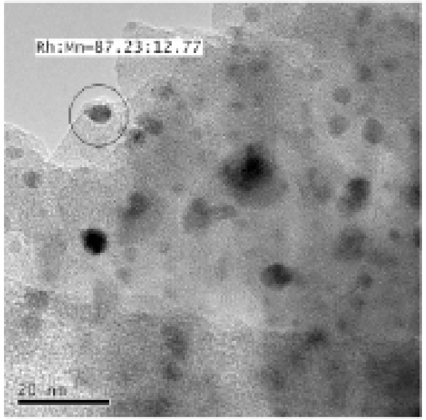
Fuel Synthesis Catalysts

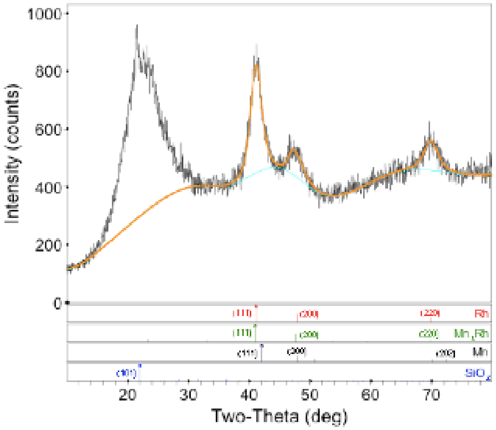
Catalyst Characterization

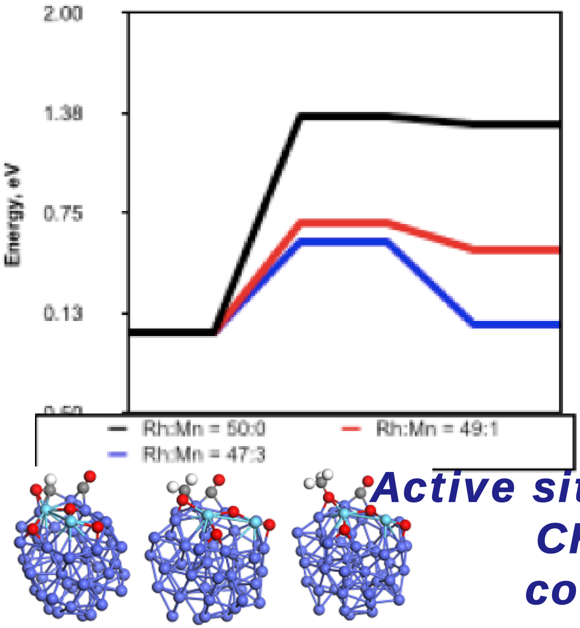
- (XRD, TEM, XPS, BET, etc.) provides snapshots of fresh, activated and spent catalysts

CRADA with DOW and Others

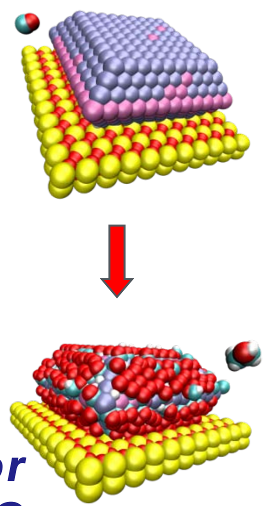
- To develop improved performance in MAS catalysts







Active sites for CH_x+CO coupling



Computational Chemistry to Improve Catalyst Performance

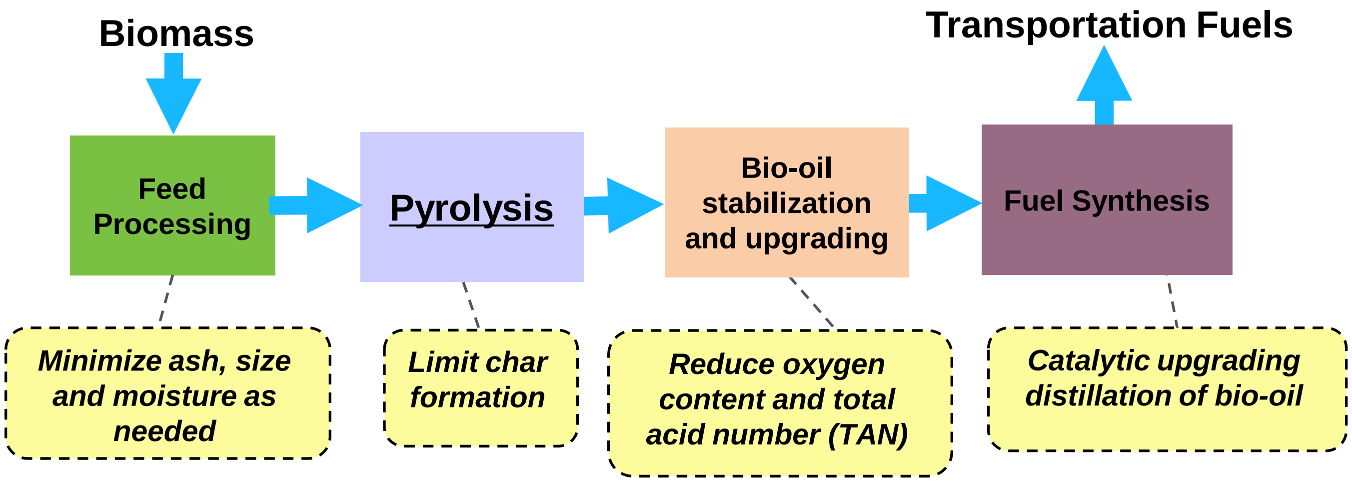
- Uses quantum theory to explain catalyst behavior
- Morphological changes of catalyst
- Interaction of catalyst with reactants, etc.

Journal of Catalysis, 271, 325-342, (2010)

Thermochemical Conversion – Fast Pyrolysis

Current Target

- By 2017, a biomass-based thermochemical route that produces gasoline and diesel blendstocks and will achieve a conversion cost of $1.56 per gallon of total blendstock ($1.47/GGE, 2007$, modeled).



Key Challenges

- Stabilizing bio-oil for > 6 months under ambient conditions
  - (Solicitation: ≤ $7.5 million, Performers: UOP, RTI, Virginia Polytechnic, Iowa State University, University Massachusetts Amherst)
- Fuel processing and operating fuel processing catalysts for ≥ 1000 hours
  - (Solicitation: ≤ $12 million, Performers: GTI, Battelle, W. R. Grace, PNNL)

Bio-oil – Technical Challenges

- Pyrolysis occurs at ambient pressure, inert atmosphere and 400 - 600 °C at reaction times approaching 0.5s
- Gives relatively high oil yields approaching 70% by weight
- Fast pyrolysis oil (bio-oil) however has many undesirable properties:
  - High water content: 15-30 wt%
  - High O content: 35-40%
  - High acidity; pH = 2.5, TAN > 100 mg KOH/g oil
  - Unstable (phase separation, reactions)
  - Low HHV: 16-19 MJ/kg
  - Distillation residue: up to 50 wt %

Energy & Fuels 18: 590-598 (2004)

Distributed Pyrolysis and Centralized Bio-Oil Processing

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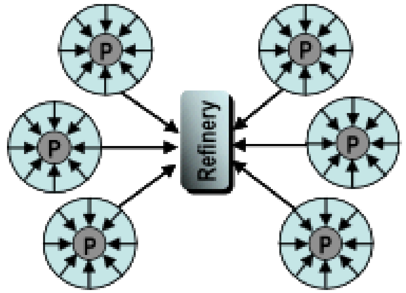
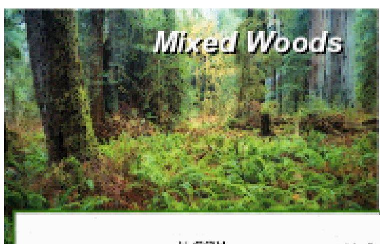
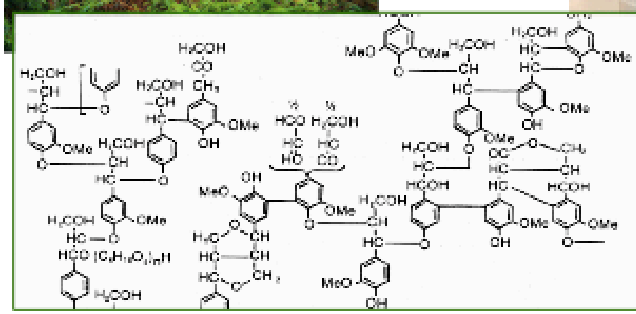


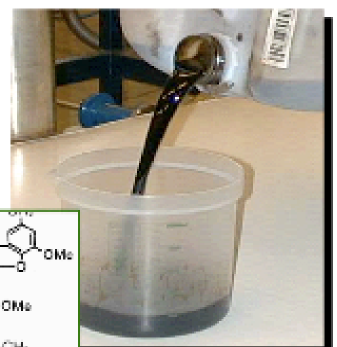
Jet-fuel fraction used to power a turbine engine jet boat

Biomass → Pyrolysis → Stabilization → Biocrude → Deoxygenate / Other Refinery Processes →

- Gasoline
- Diesel
- Jet
- Chemicals







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

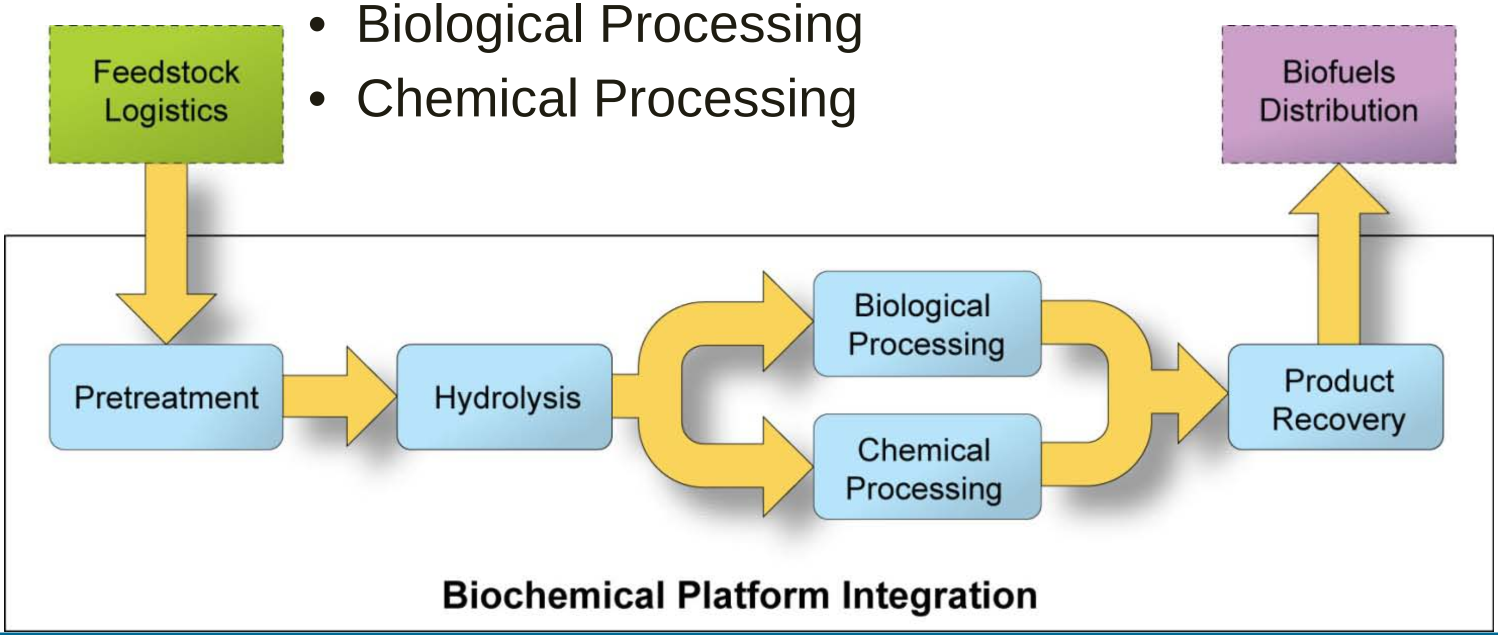
This work was developed by UOP, Ensyn, NREL and PNNL and is for fully upgraded bio-oil (TAN < 2, oxygen content < 1 wt%) that is refinery ready

Future Thrusts

- Continued bio-intermediate quality improvement and biofuel synthesis integration
- Continued conditioning/stabilizing syngas and bio-oil
- Continued drive for higher activity and selectivity, robust catalysts
- Moving towards a diverse portfolio of technologies for infrastructure compatible biofuels, requiring a need to develop:
    - ***Other thermochemical conversion of biomass routes***
    - ***Catalysts***
        - New routes need to be analyzed for potential research
        - New targets must be developed
    - ***Analysis of different entry points of bio-intermediates into existing petroleum refineries***

Biochemical Platform

- Current Target:
  - Reduce the estimated mature technology processing cost of ethanol from cellulosic feedstocks to $0.92 per gallon in 2012 (modeled)
- Major Changes:
  - Broadened unit operations to be more inclusive.
    - Biological Processing
    - Chemical Processing



High Impact Research Areas

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- **Barrier:** Low C5 sugars conversion
  - **Ethanologen Solicitation (up to $23 million)**
    - **Objective:** Drive to more robust to temperature and ethanol concentration organisms
    - **Goal:** Increase microorganism productivity and use of pentose sugars
    - **Performers:** Cargill, DuPont, Mascoma, Purdue, Verenium, NREL

- **Barrier:** High enzymatic conversion costs
  - **Enzyme Solicitation (up to $33.8 million)**
    - **Objective:** Creating highly effective, inexpensive enzyme systems for
      commercial biomass hydrolysis
    - **Goal:** Utilize pretreated cellulosic feedstocks and maximize production of glucose and xylose yields by developing a more robust enzyme
    - **Performers:** Danisco (Genencor), DSM (Sandia, Las Alamos), Novozymes, Verenium, NREL

Enzymatic Hydrolysis/ Fermentation Improvements

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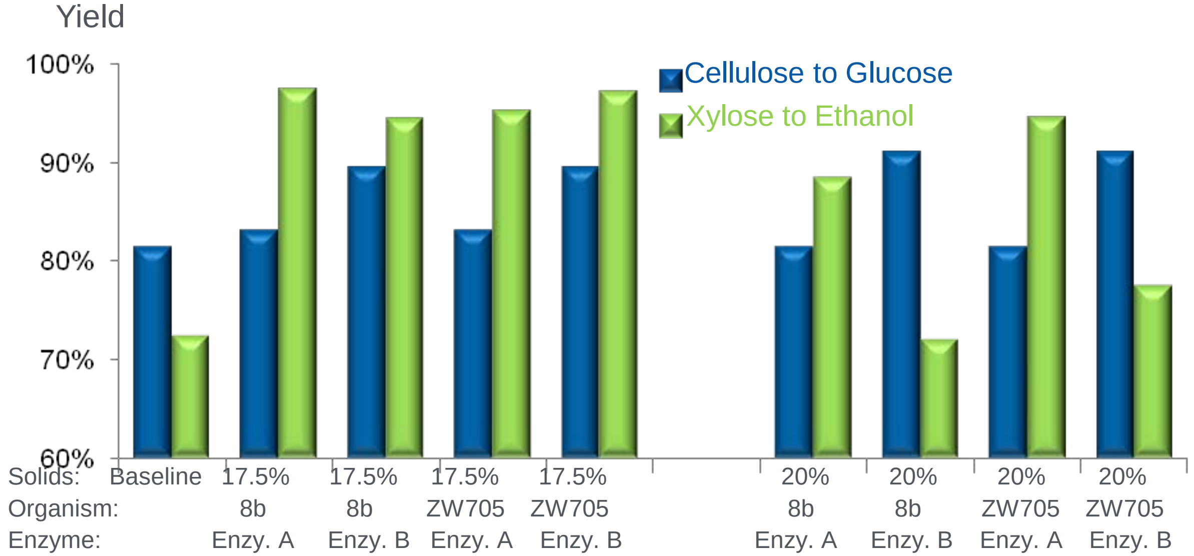
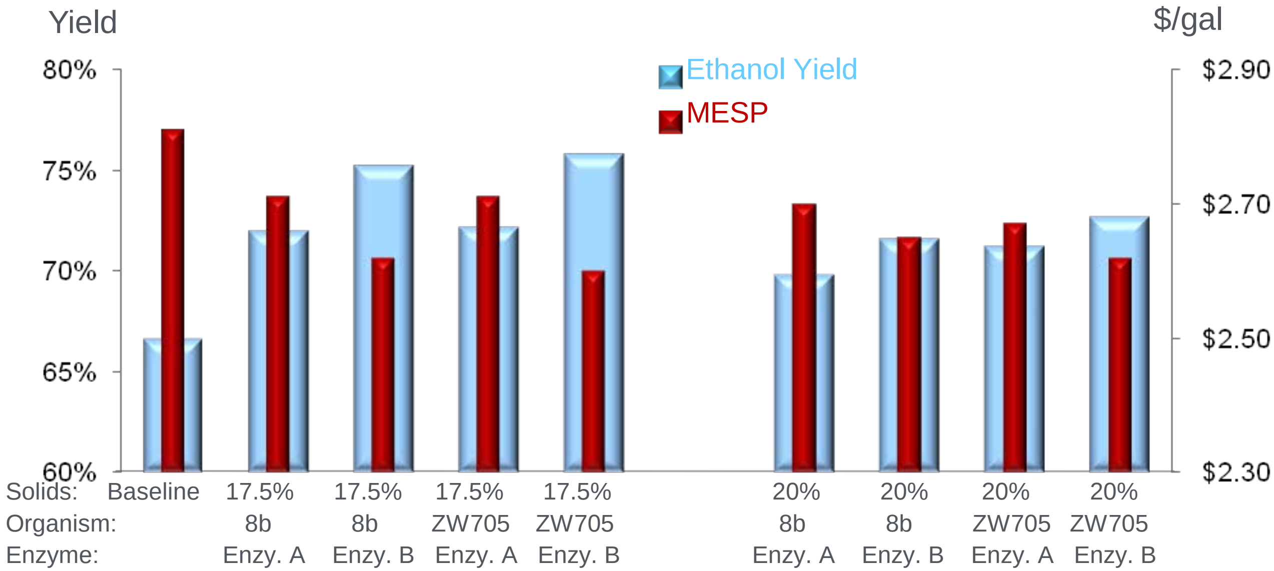


- Higher Cellulose Conversion w/ Enzyme B
- Enzyme B Insensitive to Solids Loadings

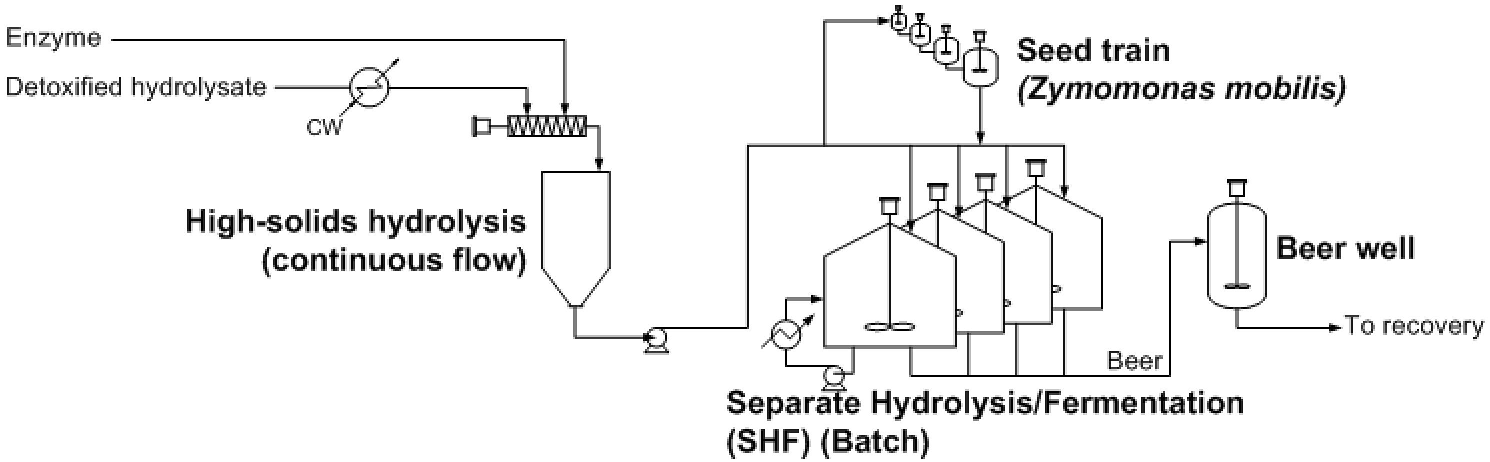
- Xylose Ferm. Improves w/new Innoc.
- Higher Xylose Conversion w/ZW705
- Strains Sensitive to Solids Loadings



- Improved Ethanol Yields in all cases
- Yield Sensitive to Solids Loading

- Improved MESP in all cases
- Solids Loading Trade-off in MESP
- 20%, ZW705, Enzyme B used in SOT

Integration



- Strict performance tables in Enzyme & Ethanologen contracts
- Validation efforts
- Biomass process integration task (NREL)
- Back end concerns (proposed switch from Lime to Ammonia Conditioning):
- Much simpler process; no solid-liquid separations required and minimal sugar losses
- Extra removal steps may be required for ammonium and sulfate coming from pretreatment, and potassium coming in with the feedstock
- The primary research plan is to reduce chemical usage in pretreatment and conditioning

Future Thrusts

- Continued pretreatment and enzyme hydrolysis integration
- Continued lowering/stabilizing enzyme costs
  - Balance with enzyme companies' marketing strategy
- Moving beyond fermentation to ethanol technologies, requiring a need to develop:
  - *Alternative fermentative organisms*
    - New routes need to be analyzed for potential research
    - New Targets must be developed
  - *Catalysts*
    - New routes need to be analyzed for potential research
    - New Targets must be developed
  - *Other bio/chemical conversion routes*

Integrated Biorefinery (IBR) Description

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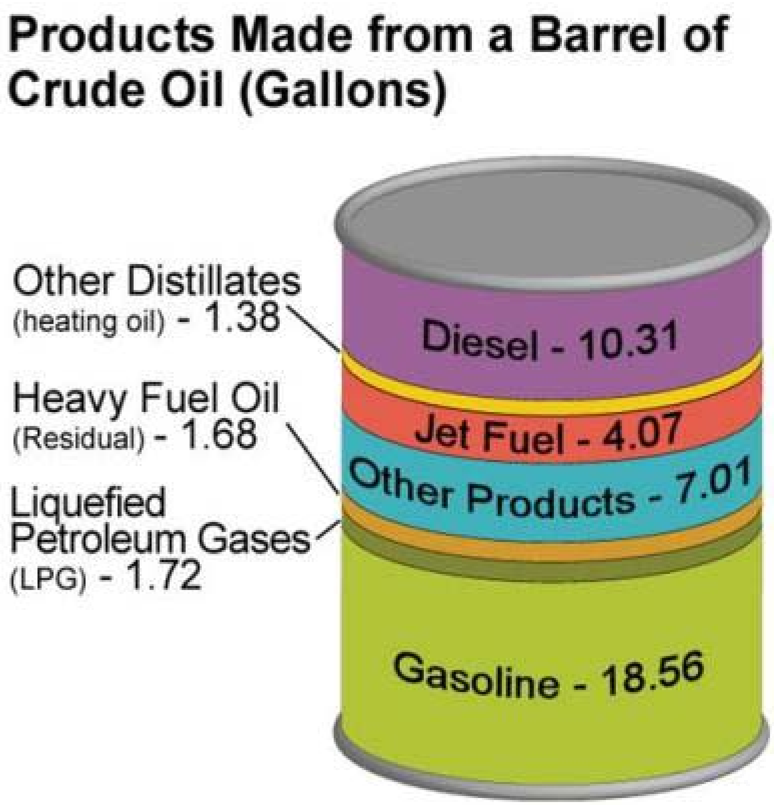
IBR Scale	Description	Feedstocks	Fuel/Product
R&D 2 projects	Includes R&D and a preliminary engineering design	Poultry Fat, Woody Biomass, Ag Residue, Algal Oil	Renewable Fuels, Renewable Gasoline, Renewable Diesel
Pilot Scale 12 projects	Processes a minimum of 1 dry tonne per day biomass and verifies the integrated performance of the given suite of technologies from both a technical and an economic perspective for the first time	Algae, CO_2, Woody Biomass, Sweet Sorghum, Corn Stover, Switchgrass, Energy Sorghum, Ag and Forestry Residue, Hybrid Poplar	Ethanol, Cellulosic Ethanol, Renewable Diesel, Jet Fuel, Renewable Diesel
Demonstration Scale 9 projects	Working with projects to verify technologies from a technical and an economic perspective at a scale sufficient for a commercial facility	Wheat Straw, Corn Stover, Poplar Residues, Woody Biomass, Algae, Mill Residues, MSW, Ag and Forestry Residue	Cellulosic Ethanol, Renewable Sulfur-Free Diesel Fuel, Renewable Hydrocarbon Based Fuel, Renewable Gasoline, Renewable Diesel, Jet Fuel, Succinic Acid
Commercial Scale 6 projects	Processes a minimum of 700 dry tonnes per day biomass and refers to a first-of-a-kind or "beta" commercial facility	Lignocellulosic Biomass, Corn Cobs, Woody Biomass, Mill Waste, Sorted MSW	Cellulosic Ethanol, Ethanol, Methanol

APPENDIX

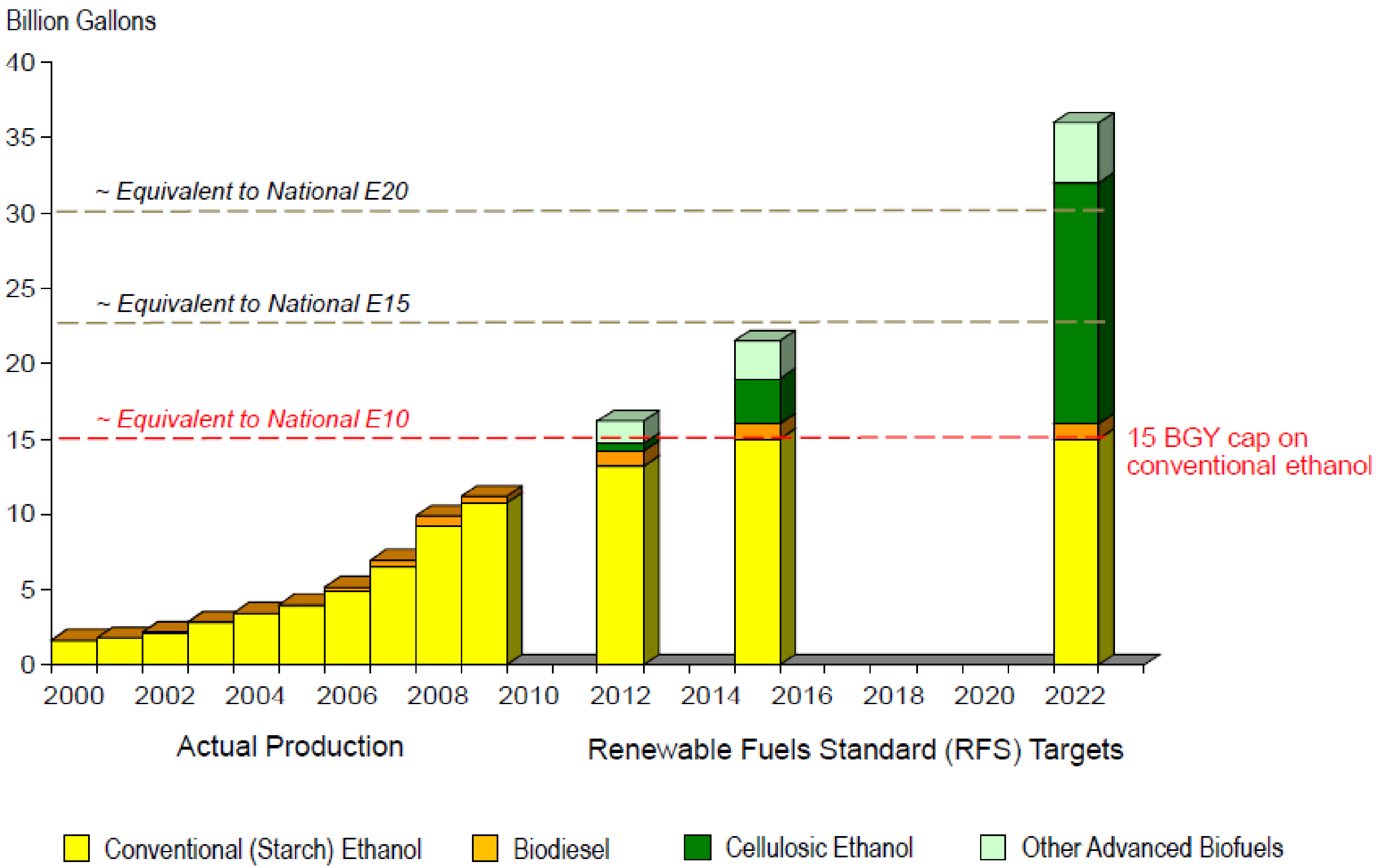
Displacing a Barrel of Crude



- Advanced biofuels and products are needed to displace the entire barrel
- Heavy duty/diesel and jet fuel substitutes are needed to displace several components of the barrel
- Cellulosic ethanol displaces light duty gasoline

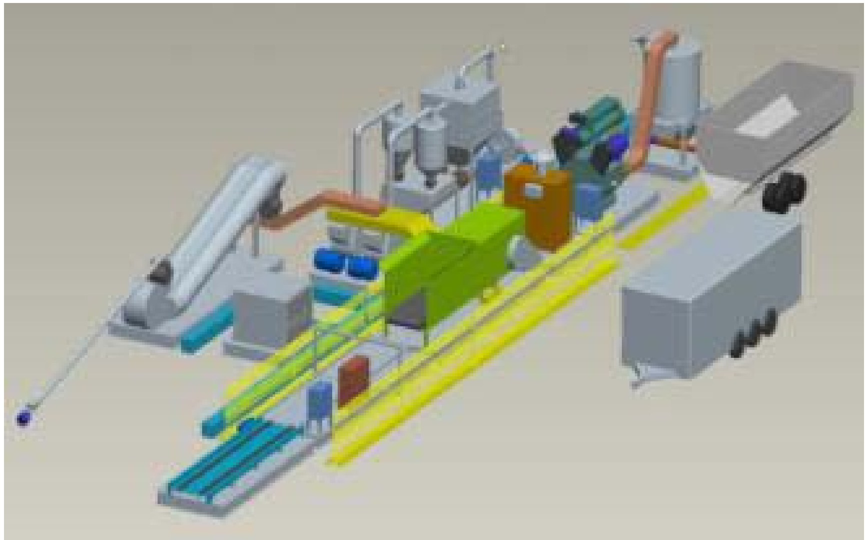
Source: Energy Information Administration, “Petroleum Explained” and AEO2009, Updated (post-ARRA), Reference Case.

EISA-Mandated U.S. Biofuels Production Targets



Feedstock Logistics

- Ongoing feedstock logistics projects are developing systems to better handle and deliver high tonnage biomass feedstocks
- Five projects were selected in August 2009 to work on agricultural residues, woody biomass, and energy crops
- Development of the Deployable Process Demonstration Unit (PDU) will help bridge gap between producers and refineries
  - Will test supply system concepts, new equipment designs, and deploy new technologies
  - Produce engineered feedstocks to meet commodity-scale performance metrics and advanced conversion characteristics



FY10 Accomplishments

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Biochemical Platform State of Technology

	2007	2008	2009	2010	2011	2012
Minimum Ethanol Selling Price ($/gal)	$2.69	$2.61	$2.40	$1.92	$1.68	$1.49
Feedstock Contribution ($/gal)	$0.97	$0.90	$0.81	$0.64	$0.60	$0.57
Conversion Contribution ($/gal)	$1.72	$1.71	$1.59	$1.28	$1.08	$0.92
Yield (Gallon/dry ton)	72	73	77	83	87	90
Feedstock						
Feedstock Cost ($/dry ton)	$69.60	$65.30	$62.05	$53.70	$52.00	$50.90
Pretreatment						
Solids Loading (wt%)	30%	30%	30%	30%	30%	30%
Xylan to Xylose (including enzymatic)	75%	75%	84%	85%	88%	90%
Xylan to Degradation Products	13%	11%	6%	6%	5%	5%
Conditioning						
Ammonia Loading (mL per L Hydrolyzate)	50	50	38	38	35	25
Hydrolyzate solid-liquid separation	yes	yes	yes	yes	yes	no
Xylose Sugar Loss	2%	2%	2%	2%	1%	1%
Glucose Sugar Loss	1%	1%	1%	1%	1%	0%
Enzymes						
Enzyme Contribution ($/gal EtOH)	$0.35	$0.35	$0.35	$0.17	$0.12	$0.12
Enzymatic Hydrolysis & Fermentation						
Total Solids Loading (wt%)	20%	20%	20%	20%	20%	20%
Combined Saccharification & Fermentation Time (d)	7	7	7	5	3	3
Corn Steep Liquor Loading (wt%)	1%	1%	1%	1%	0.60%	0.25%
Overall Cellulose to Ethanol	85%	85%	84%	85%	85%	85%
Xylose to Ethanol	76%	80%	82%	82%	85%	85%
Minor Sugars to Ethanol	0%	0%	51% (arab.)	80%	85%	85%

Gasification: State of Technology and Projection

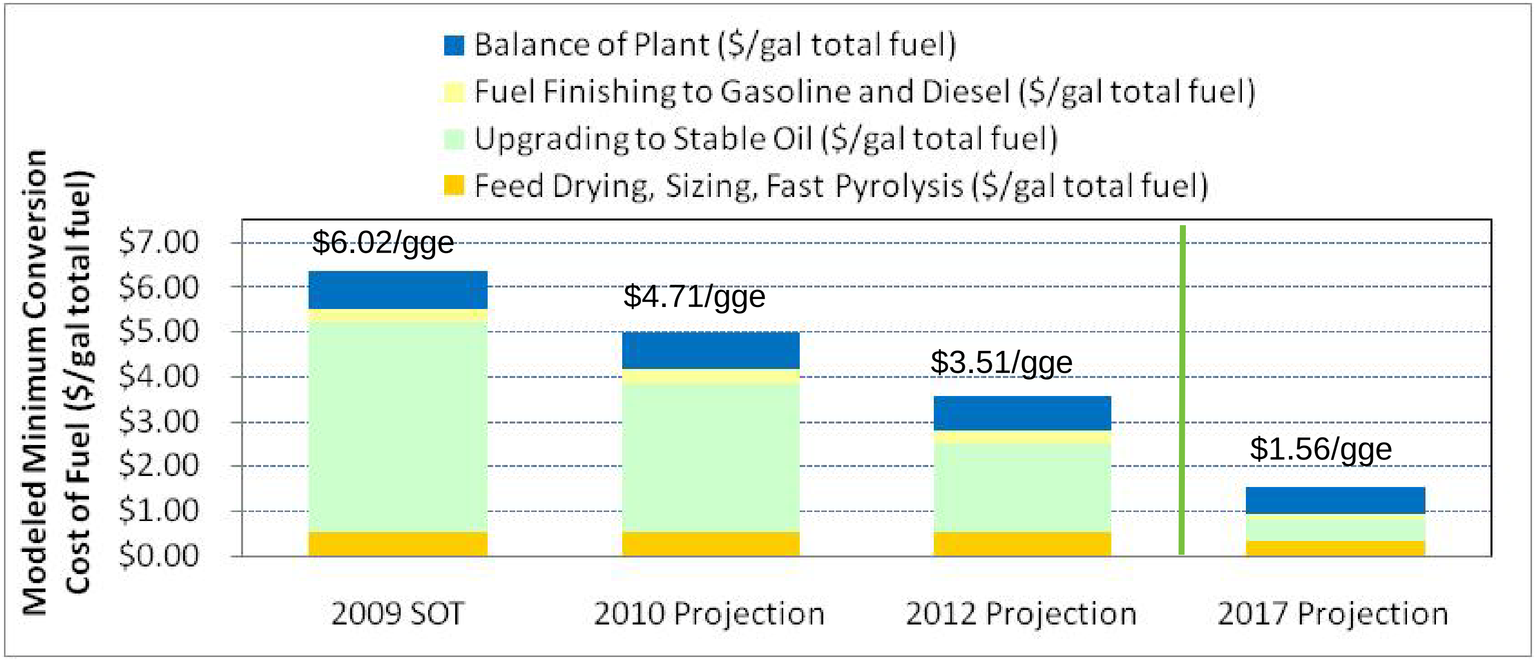
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

	2005	2007	2008	2009	2010	2011	2012
Minimum Ethanol Selling Price ($/gal)	$3.47	$3.57	$2.40	$2.26	$1.90	$1.70	$1.57
Feedstock Contribution ($/gal)	$1.58	$1.58	$1.05	$0.95	$0.80	$0.73	$0.71
Conversion Contribution ($/gal)	$1.89	$1.89	$1.35	$1.31	$1.10	$0.97	$0.86
Ethanol Yield (Gallon/dry ton)	43	43	61	62	68	71	71
Mixed Alcohol Yield (Gallon/dry ton)	50	50	71	72	80	84	84
Feedstock							
Feedstock Cost ($/dry ton)	$67.55	$67.55	$63.50	$58.20	$54.20	$51.80	$50.70
Syngas Generation							
Syngas Yield (lb/lb dry feed)	0.82	0.82	0.82	0.82	0.82	0.82	0.82
CH_4 Concentration in raw syngas(mol %-dry basis)	15.1	15.1	15.1	15.1	15.1	15.1	15.1
Syngas Cleanup and Conditioning							
Tar Reformer – CH_4 conversion (%)	20	20	50	56	80	80	80
Tar Reformer – Benzene conversion (%)	70	80	98	90	99	99	99
Tar Reformer – Total Tar conversion (%)	95	97	97	97	99.9	99.9	99.9
Tar Reformer – Exit CH_4 concentration (mol %)	10.2	10.2	3.8	3.1	1.1	1.3	1.3
Catalytic Fuel Synthesis							
Compression for fuel synthesis (psia)	2000	2000	2000	1500	1500	1500	1500
Single pass CO conversion (%)	40	40	40	40	40	50	50
Overall CO conversion (%)	40	40	40	40	40	50	50
CO Selectivity to alcohols - CO_2 free basis (%)	80	80	80	80	80	80	80
Total Alcohol Productivity (g/kg/hr)	300	300	300	300	450	600	600

Major Focus 2005-2010 (Single Pass)

Major Focus 2009-2012

Fast Pyrolysis: State of Technology and Projections



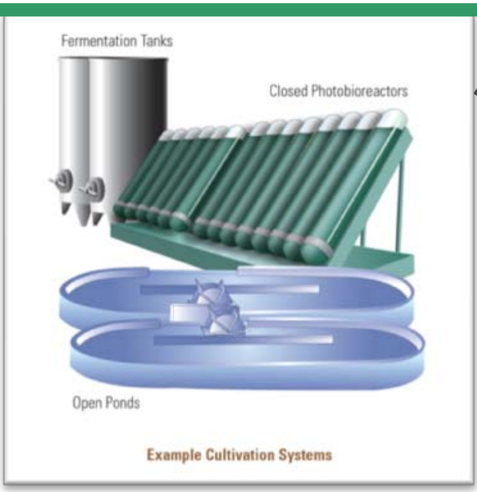
	2009 SOT	2010 Projection	2012 Projection	2017 Projection
Conversion Contribution ($/gal gasoline)	**$6.30**	**$4.92**	**$3.51**	**$1.56**
Conversion Contribution ($/gal diesel)	**$6.37**	**$4.99**	**$3.57**	**$1.56**
Conversion Contribution ($/gge total fuel)	**$6.02**	**$4.71**	**$3.38**	**$1.48**
Feed Drying, Sizing, Fast Pyrolysis ($/gal total fuel)	$0.54	$0.53	$0.52	$0.34
Upgrading to Stable Oil ($/gal total fuel)	$4.69	$3.34	$2.01	$0.46
Fuel Finishing to Gasoline and Diesel ($/gal total fuel)	$0.30	$0.29	$0.29	$0.12
Balance of Plant ($/gal total fuel)	$0.82	$0.81	$0.74	$0.64

Current stakeholders: NREL, PNNL, INL, ORNL, Univ. of Massachusetts Amherst, Univ. of Purdue, RTI, UOP, Iowa State Univ., Virginia Polytechnic Institute.

Algal Biofuel Systems: Technical Challenges

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

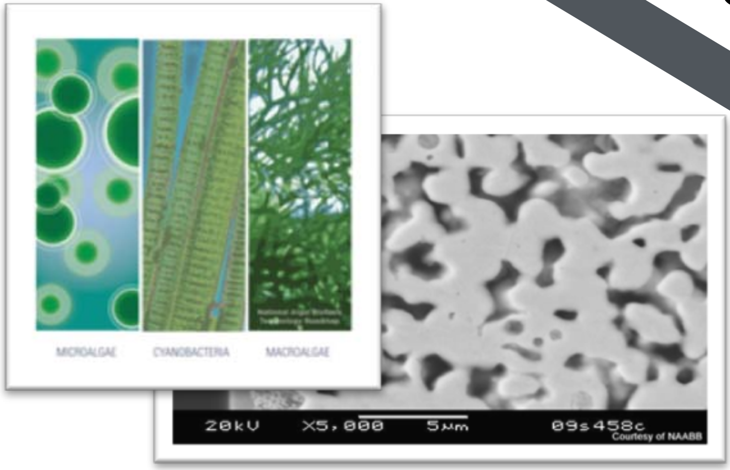
Biology and Cultivation



- Cultivation system design
- Temperature Control
- Invasion and fouling
- Cultures
- Growth, stability, and resilience
- 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.

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

Conversion and End-use

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

Integrated Biorefineries

- **29 R&D, pilot, demonstration and commercial scale projects selected to validate IBR technologies**
- **More than 15 types of feedstocks represented**

- Poultry Fat
- Woody Biomass
- Ag Residue
- Algal Oil
- Algae
- CO_2

- Sweet Sorghum
- Corn Stover
- Switchgrass
- Energy Sorghum
- Forestry Residue
- Hybrid Poplar

- Wheat Straw
- Poplar Residues
- Mill Residues
- Municipal Solid Waste
- Lignocellulosic Biomass
- Corn Cobs

- **Several different types of fuels and products will be developed**

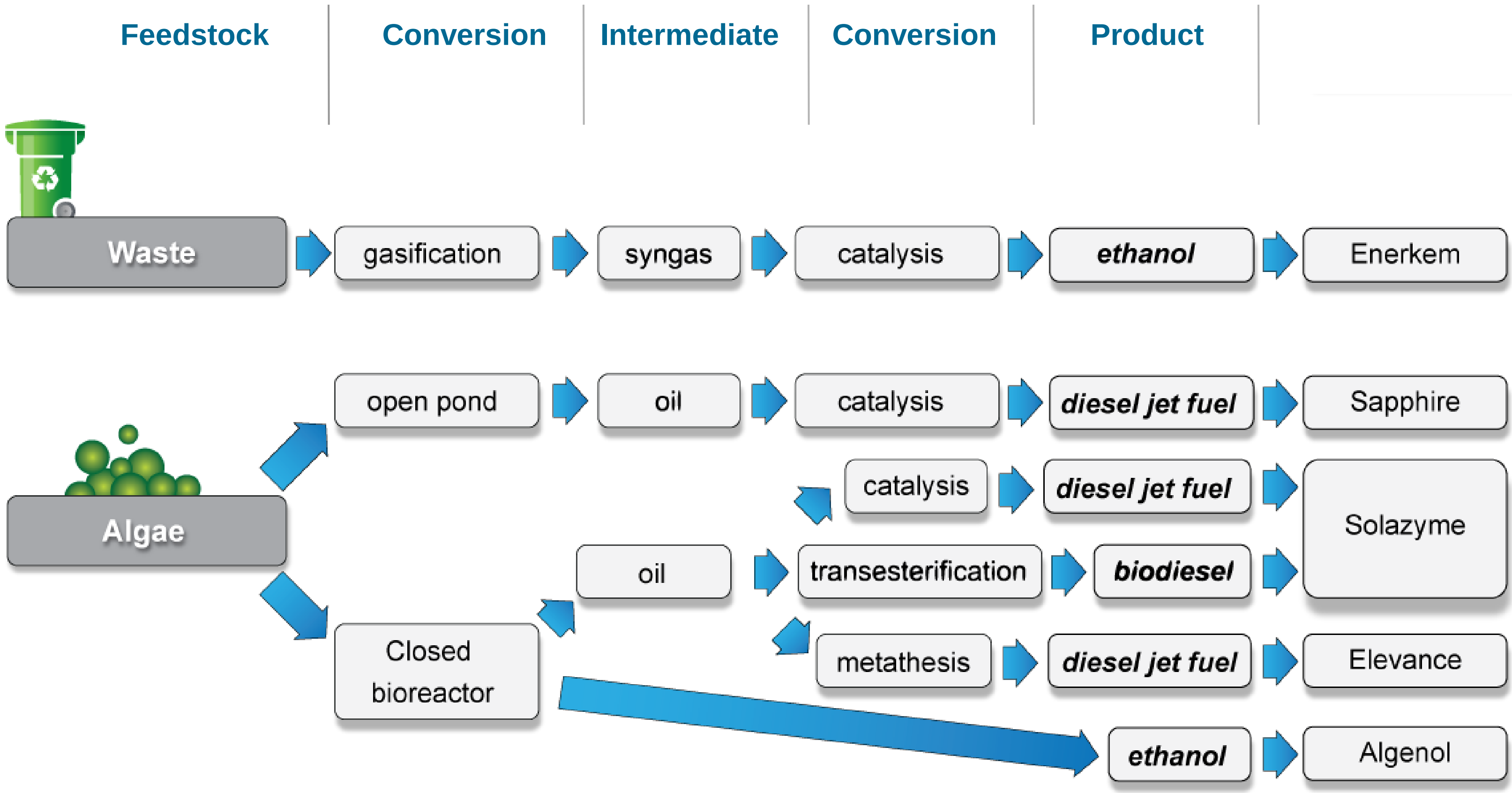
- Ethanol
- Cellulosic Ethanol
- Methanol

- Renewable Gasoline
- Renewable Diesel
- Jet Fuel

- Renewable Sulfur-Free Diesel
- Succinic Acid

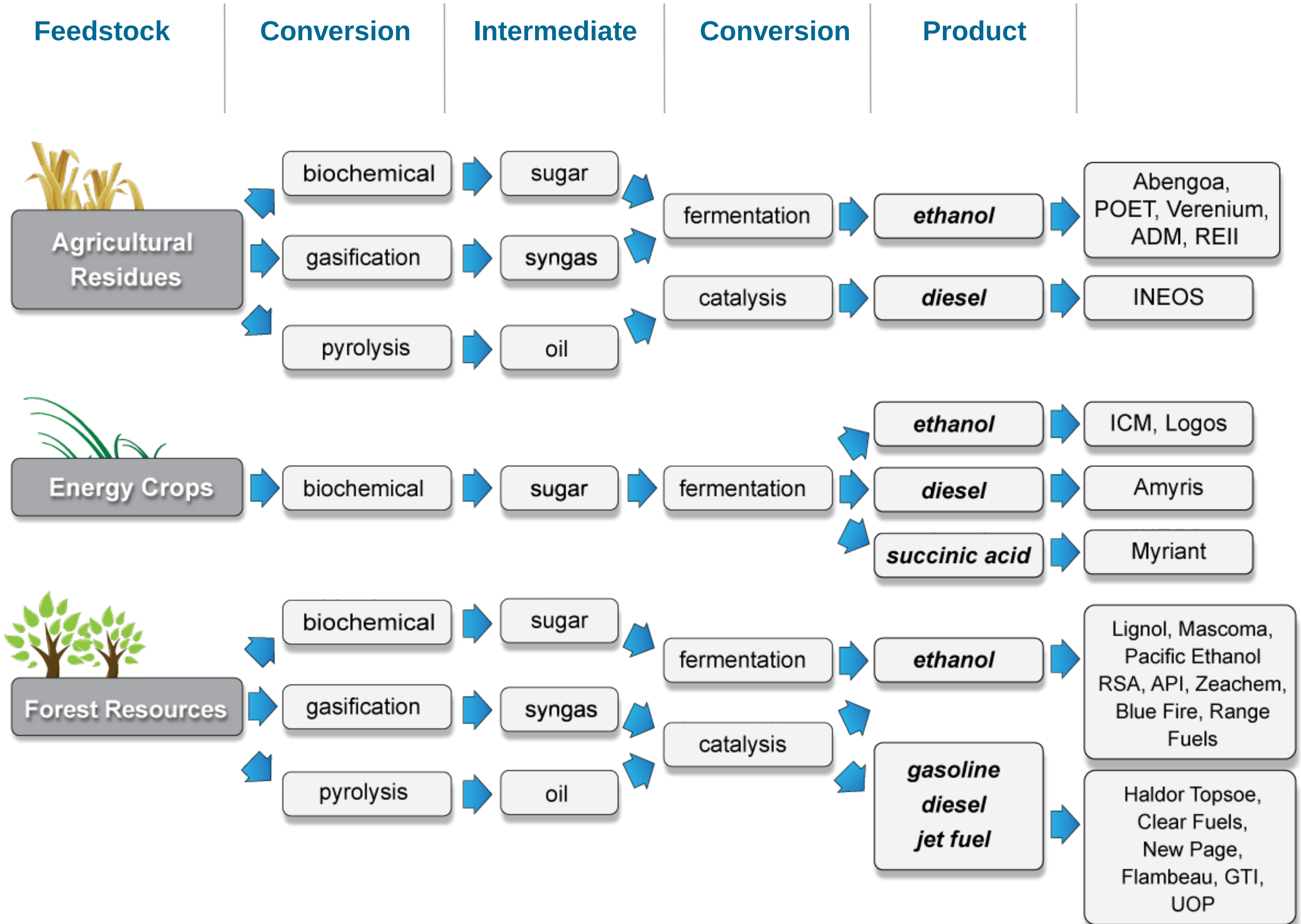
Integrated Biorefinery Pathways

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



Integrated Biorefinery Pathways

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy



Launch a new DOE initiative to accelerate, develop and deploy advanced biopower technologies over the next six years. Initiative will establish partnerships with industry and support efforts to:

•Conduct RD&D on advanced pretreatment and conversion technologies leading to greater percentage biomass co-firing with coal to

•increase overall efficiency

•improve environmental performance

•decrease cost of biopower electricity

•Support pilot scale projects up to 30 MW

•Demonstrate utility scale, biomass repowering with co-firing of up to 20 percent biomass by 2016

Our Commitment to Sustainability

Develop and invest in bioenergy resources, technologies, and systems that enhance the health of our environment, economy, and communities.

Environmental Sustainability | **Economic Sustainability** | **Social Sustainability**

Biomass-to-Bioenergy Supply Chain

Feedstocks
- Evaluate nutrient and carbon cycling
- Assess impact on land and resource use

Conversion
- Minimize water consumption and air pollution
- Maximize efficiency

Distribution
- Reduce carbon footprint of new facilities
- Utilize co-products and fully integrate systems

End Use
- Ensure minimal greenhouse gas emissions
- Avoid negative impacts on human health

Cross cutting
- Life cycle analysis of water consumption and GHG emissions
- Land use change modeling
- Water quality analysis

National Advanced Biofuels Consortium

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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.

ARRA Funded: - 3 year effort
- DOE Funding $33.8M
- Cost Share $12.5M

Total $46.3M

Consortium Leads:

National Renewable Energy Laboratory
Pacific Northwest National Laboratory

Consortium Partners:

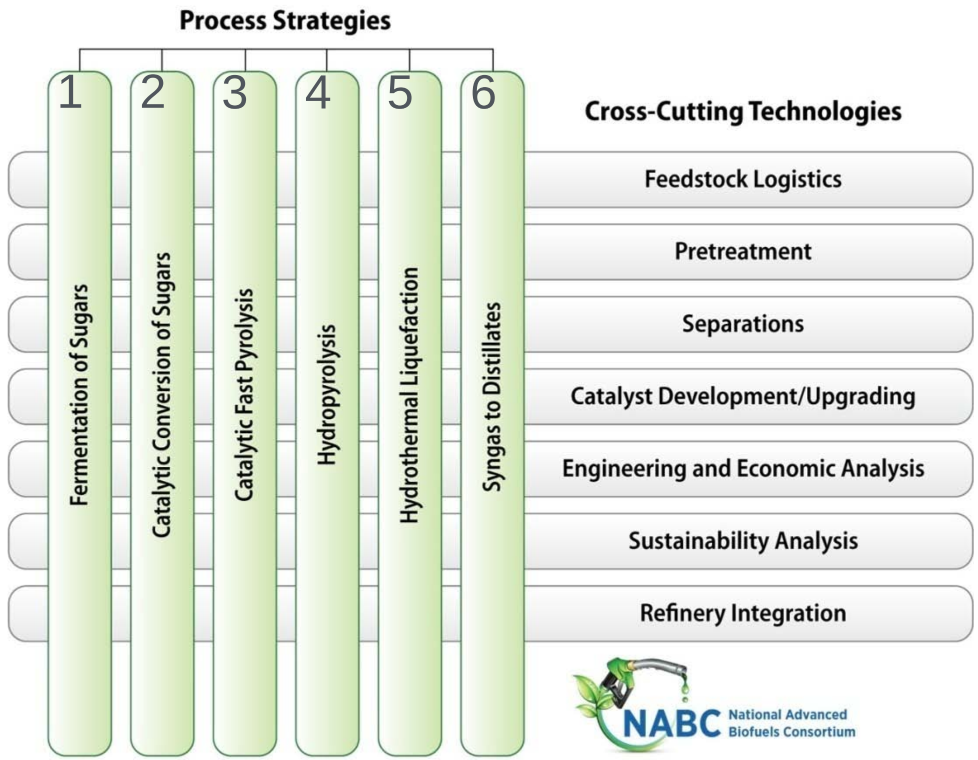
Albemarle Corporation
Amyris Biotechnologies
Argonne National Laboratory
BP Products North America Inc.
Catchlight Energy, LLC
Colorado School of Mines
Iowa State University
Los Alamos National Laboratory
Pall Corporation
RTI International
Tesoro Companies Inc.
University of California, Davis
UOP, LLC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

NABC Research Strategies

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.

ARRA Funded: DOE Funding $33.8M/Cost Share $12.5M over 3 years

NABC matrix of technology and strategy teams will ensure development of complete integrated processes.



Consortium Leads: NREL, PNNL

Consortium Partners: Albemarle, Amyris, ANL, BP Products, Catchlight, Colorado School of Mines, Iowa State Univ., LANL, Pall, RTI, Tesoro, UC Davis, UOP, Virent, Washington State Univ.

NABC Barriers

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Six Initial Strategies Proposed By NABC

Strategy	State of Technology	Barriers for Lignocellulosic Feedstocks
1) Fermentation of sugars	Fermentation-derived product from traditional sugars; upon upgrading meets ASTM specifications for #2 diesel	Clean, low cost, biomass sugars C5 conversion to products Organism robustness and productivity
2) Catalytic conversion of sugars	Gasoline product from traditional sugars via aqueous-phase catalytic route	Clean, low cost, biomass sugars Catalyst performance mixed sugar streams Catalyst life (poisoning by lignin/proteins)
3) Catalytic fast pyrolysis	Upgrading of thermal fast pyrolysis oil to gasoline, jet fuel, and diesel	Selective oxygen removal Catalyst coking; char and metal separations Undetermined product quality
4) Hydropyrolysis	Production of bio-oil with improved properties	High hydrogen use Selectivity to oil vs. hydrocarbon gases Catalyst life
5) Hydrothermal liquefaction	Characterization of oil and demonstrated upgrading potential	Reaction Severity (pressure, temperature) High viscosity of oil Char and metal separations
6) Syngas-to-distillates	Complex, multi-step (MTG); Note: our project examines a 1-step alternative process	Capital cost Catalyst activity and selectivity Development of multifunctional catalysts

- Each of the six strategies comprises multiple processing pathways that address key technology barriers which can be combined in innovative ways to meet the objectives of the project.
- The NABC brings together a cross-disciplinary team with a diverse skill set to carry out targeted research.

EISA Mandated Production Targets

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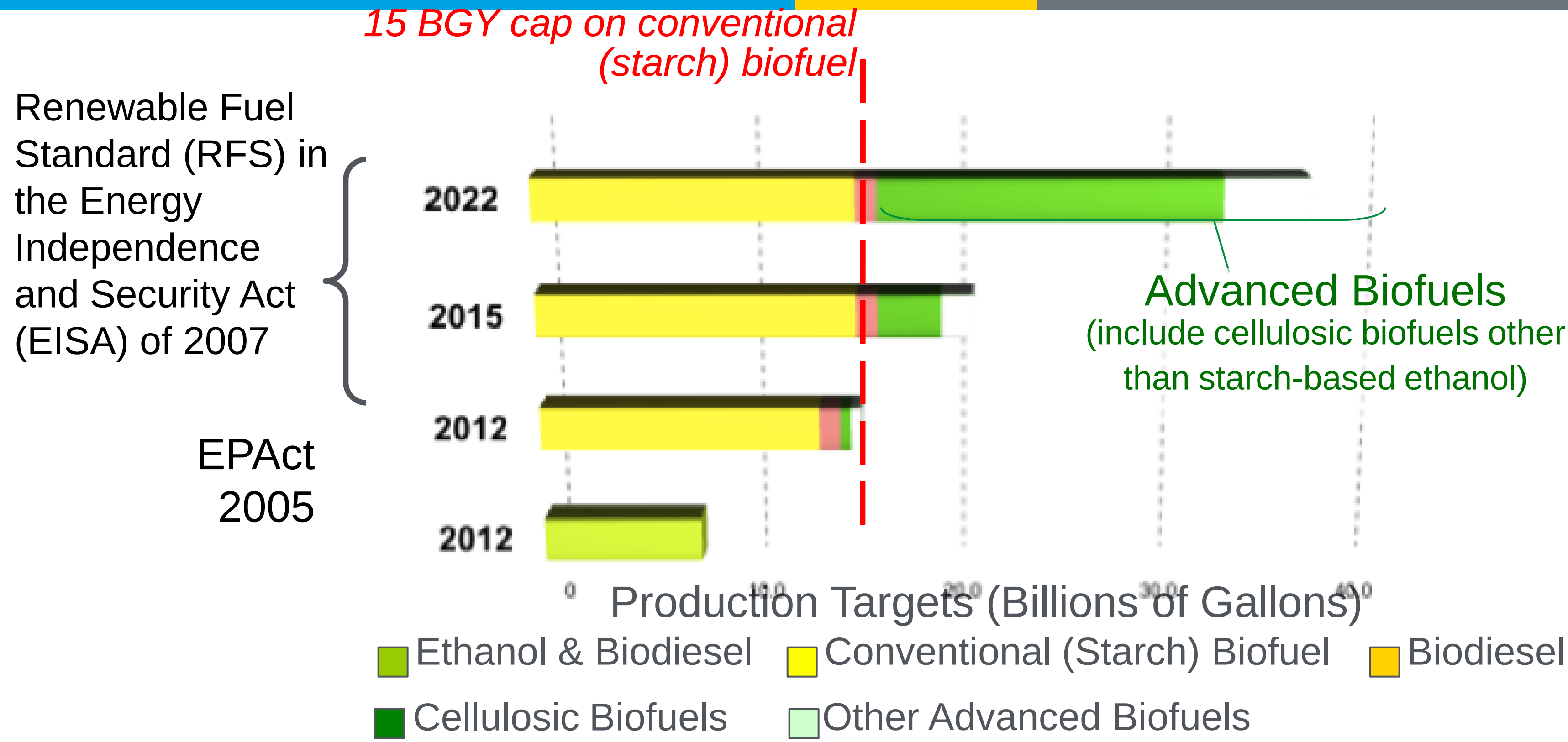

EISA defines *Advanced Biofuel* as “renewable fuel, other than ethanol derived from corn starch, that has lifecycle greenhouse gas emissions…that are *at least 50 percent less* than baseline lifecycle greenhouse gas emissions.”

Cellulosic ethanol technology is important to reaching the 2022 EISA target, however, other advanced biofuels will be needed to aid in this endeavor.

Where We Are Going

The Nation's Goal:

36 billion gallons (136 billion liters)/year of biofuels by 2022

DOE's path forward:

- Integrated programs R&D to solve technical barriers
  - Applied research for short- and mid-term impact
  - Fundamental research for longer-term impact
- Cost-shared programs with industry to reduce risk
- Broadening portfolio to maximize volumetric production

Sustainability is highly important in all aspects of our work