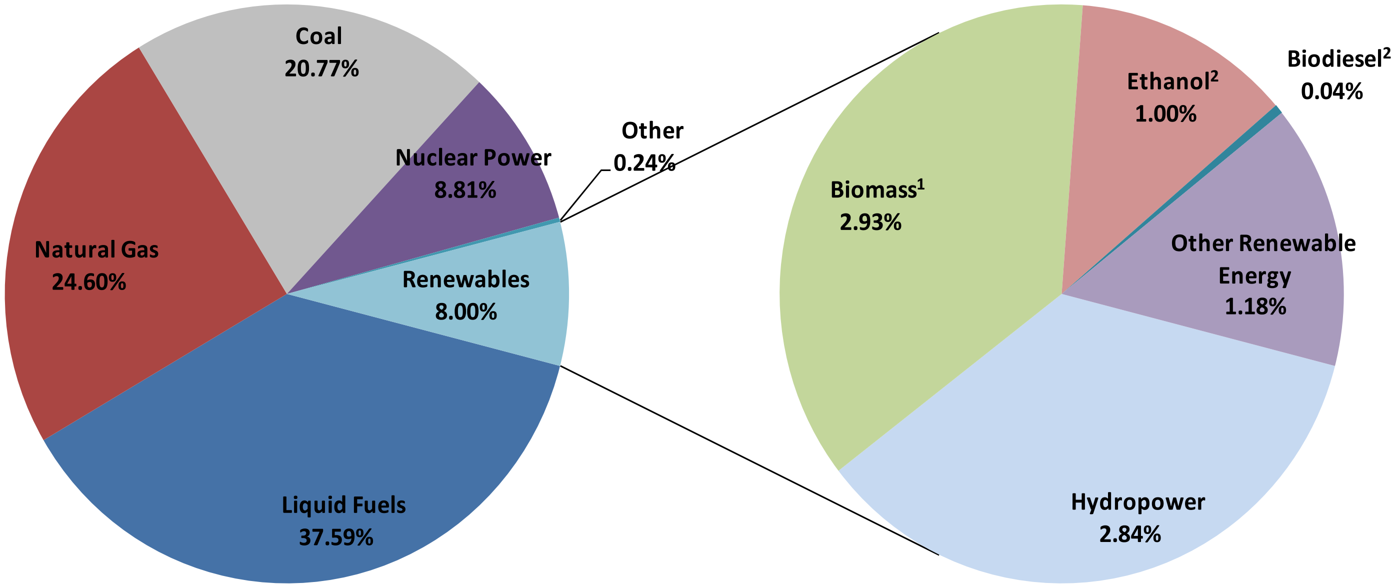
NREL National Renewable Energy Laboratory
Innovation for Our Energy Future

NREL Thermochemical Research Program and Facilities

Task 33 Meeting
12April, 2011

Richard Bain

U.S. Primary Energy Consumption in 2009

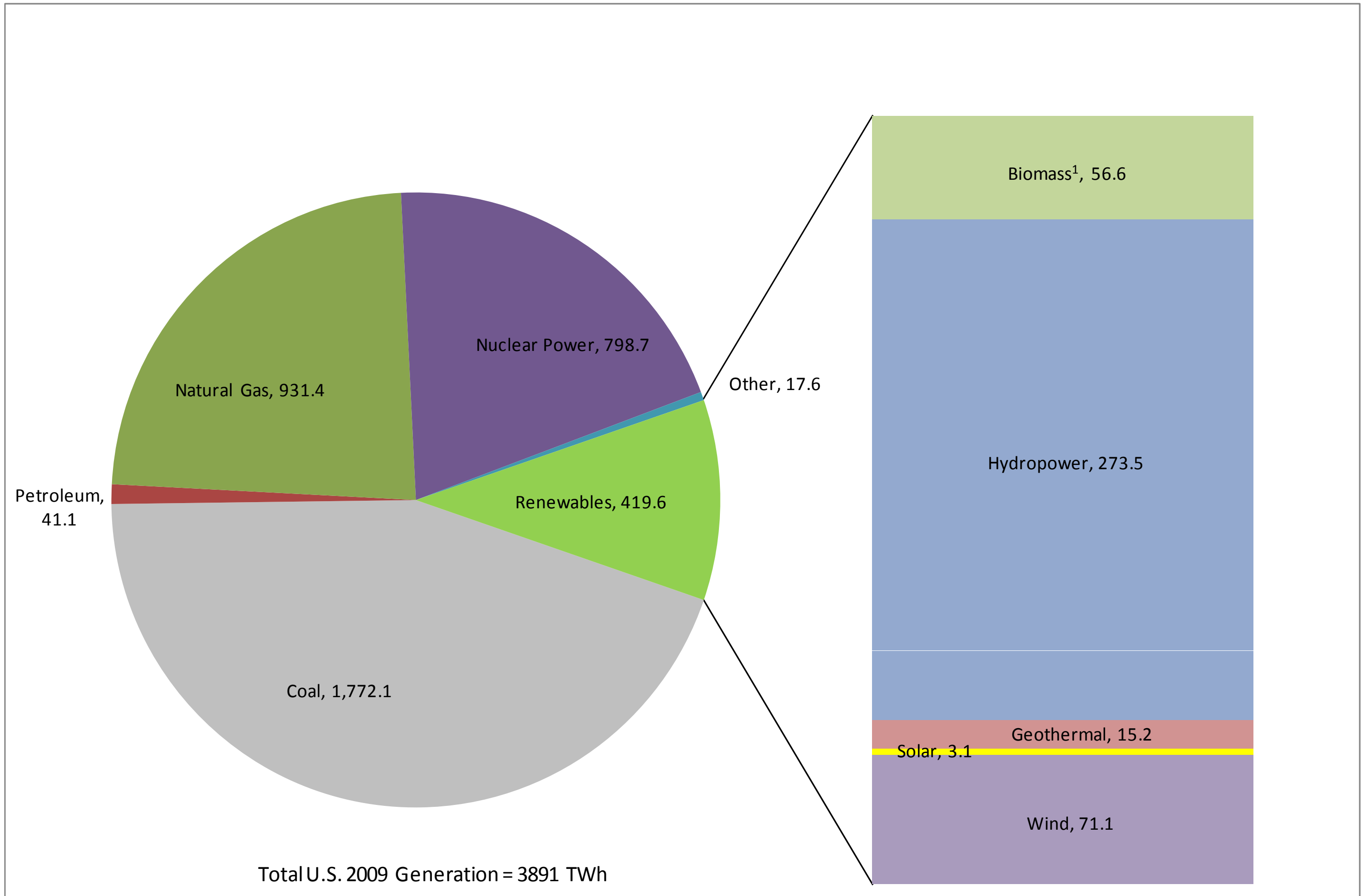


[1] Biomass modified to include biogenic MSW and landfill gas included in other/other renewables in AEO

[2] Ethanol and biodiesel taken from Liquid Fuels in AEO

Total U.S. 2009 Primary Energy Consumption = 100 Exajoules

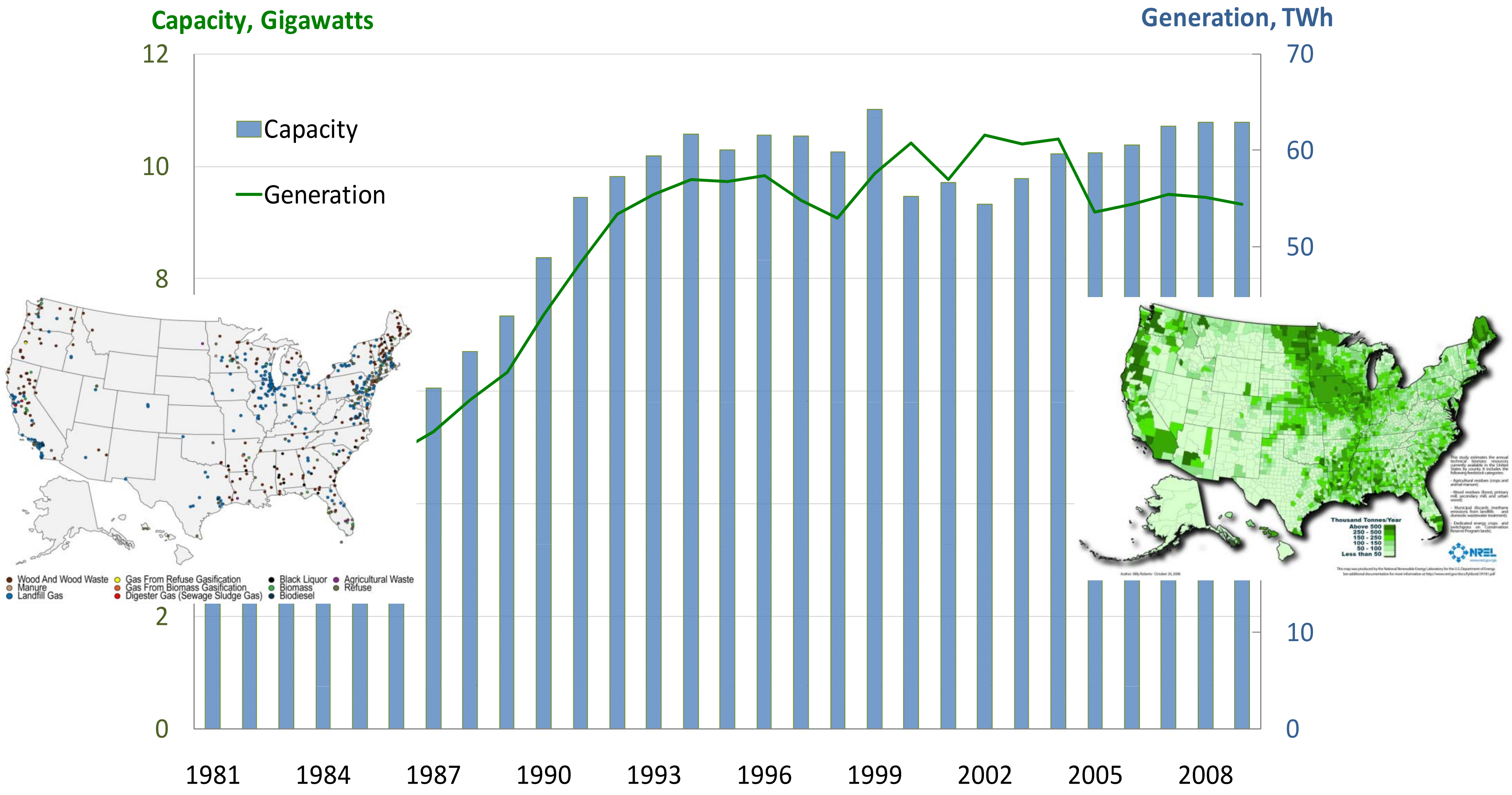
U.S. Electricity Generation in 2009



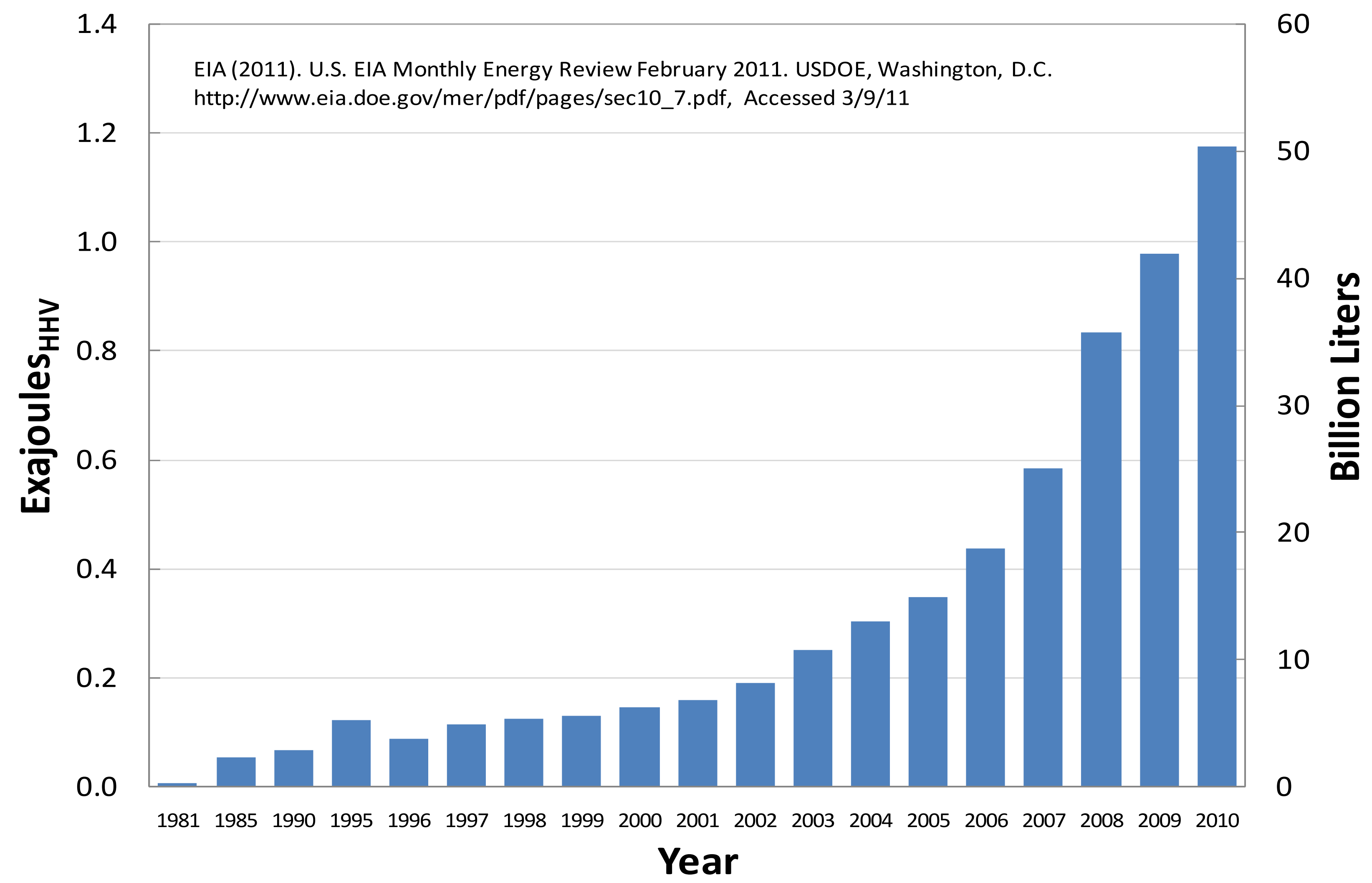
Total U.S. 2009 Generation = 3891 TWh

[1] Biomass includes traditional biomass, biogenic MSW, and landfill gas generation

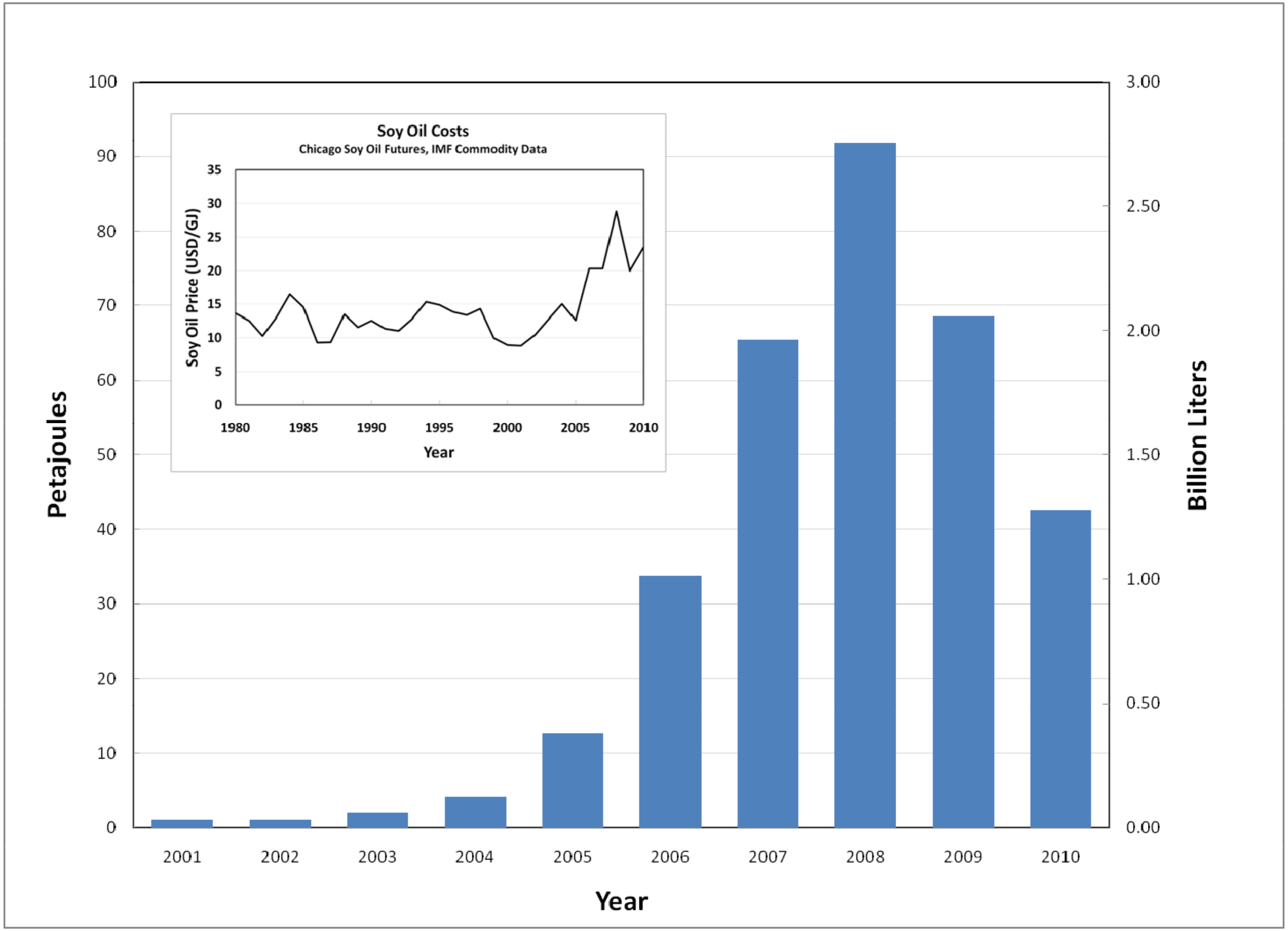
Historical Biopower Capacity and Generation



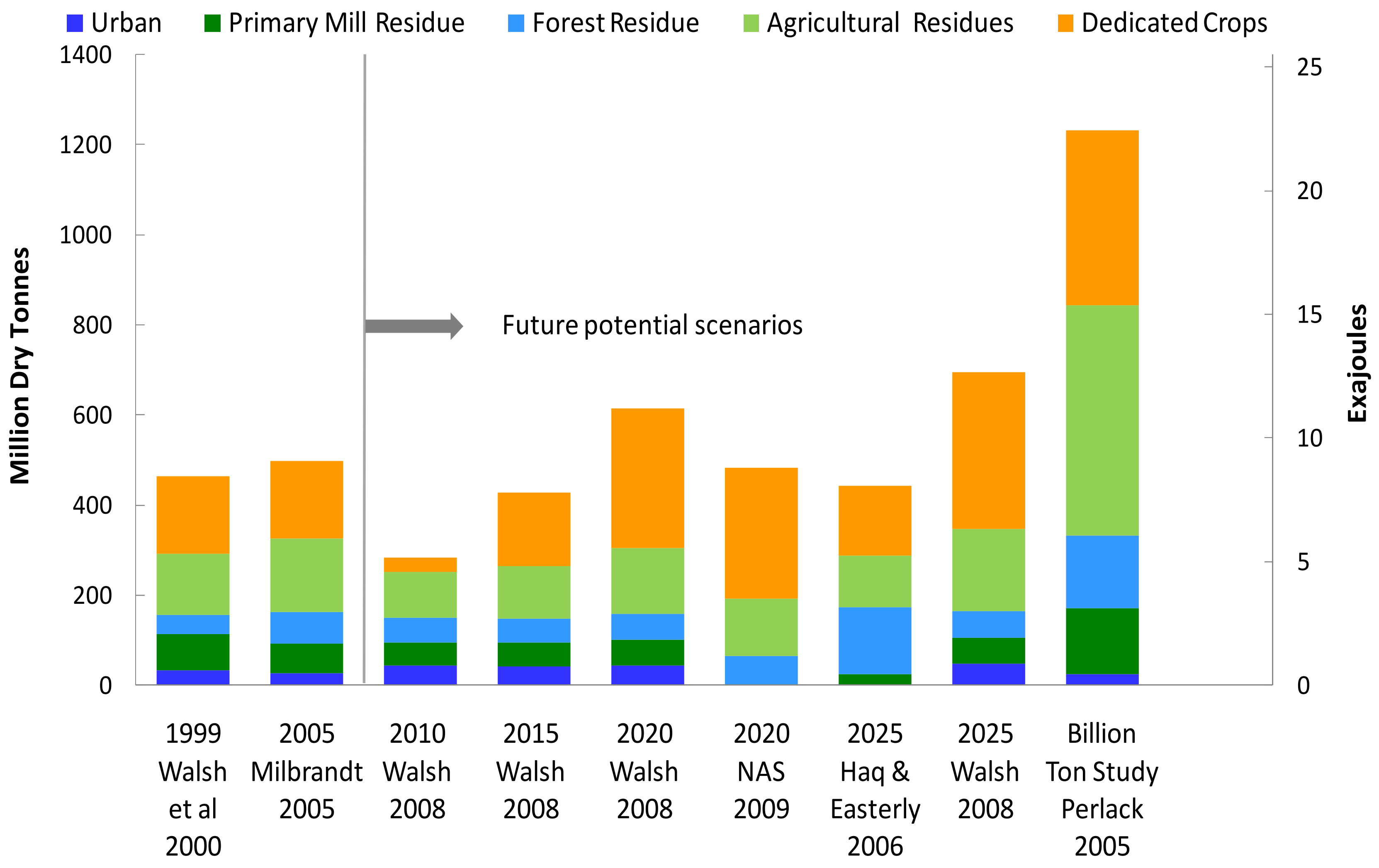
Historical U.S. Ethanol Production



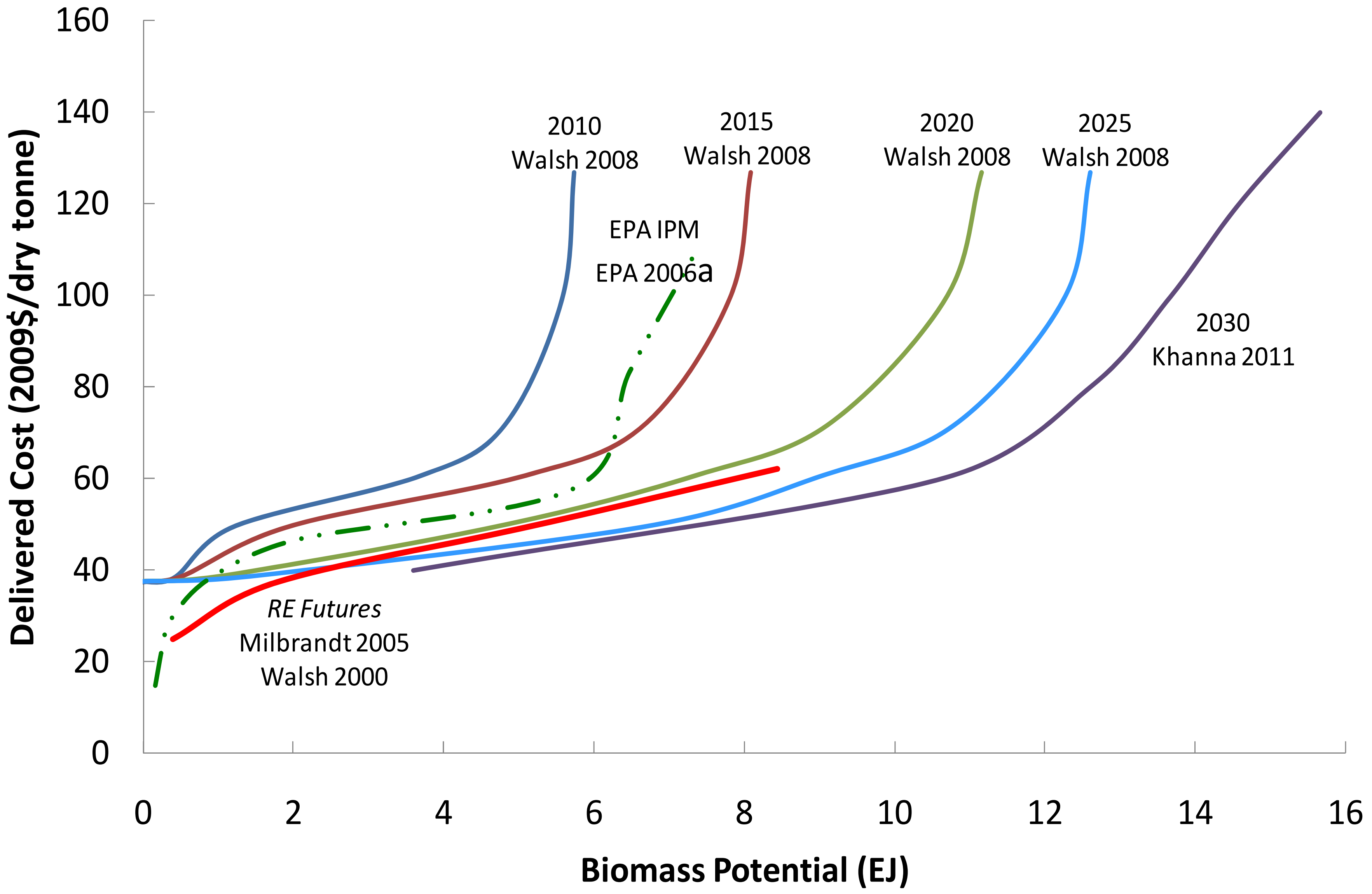
Historical U.S. Biodiesel Production



U.S. Biomass Resource Potential Scenarios



U. S. Biomass Supply Curve Scenarios



NREL BIOFUELS PLATFORM: GOALS

Near-term Goal: Demonstrate a Modeled, Cost Competitive, Biomass Derived Ethanol Price by 2012

- Process Target: Integrated bioethanol technology demonstrated at pilot scale (1 ton per day)
- Cost Target: Data from integrated pilot operation combined with process design model & cost estimate validates an ~$1.50/gal MESP
- R&D Plan: Well-defined R&D plan in place with multiple paths to success for both biochemical and **thermochemical** conversion

Longer Term Goal: Demonstrate Other Biofuels Technologies That Can Contribute to Larger Volume EISA Targets

- Process Target: Development of alternate feedstock processes
  Continue to pursue technology advances targeting cost reduction
  Progress alternative fuel processes ("Energy Dense/Infrastructure Compatible")
- Cost Target: Multiple cost-competitive biomass to fuel options with the potential to displace gasoline, diesel and/or jet fuel
- R&D Plan: Develop core research plan that complements advanced biofuels and algae consortia

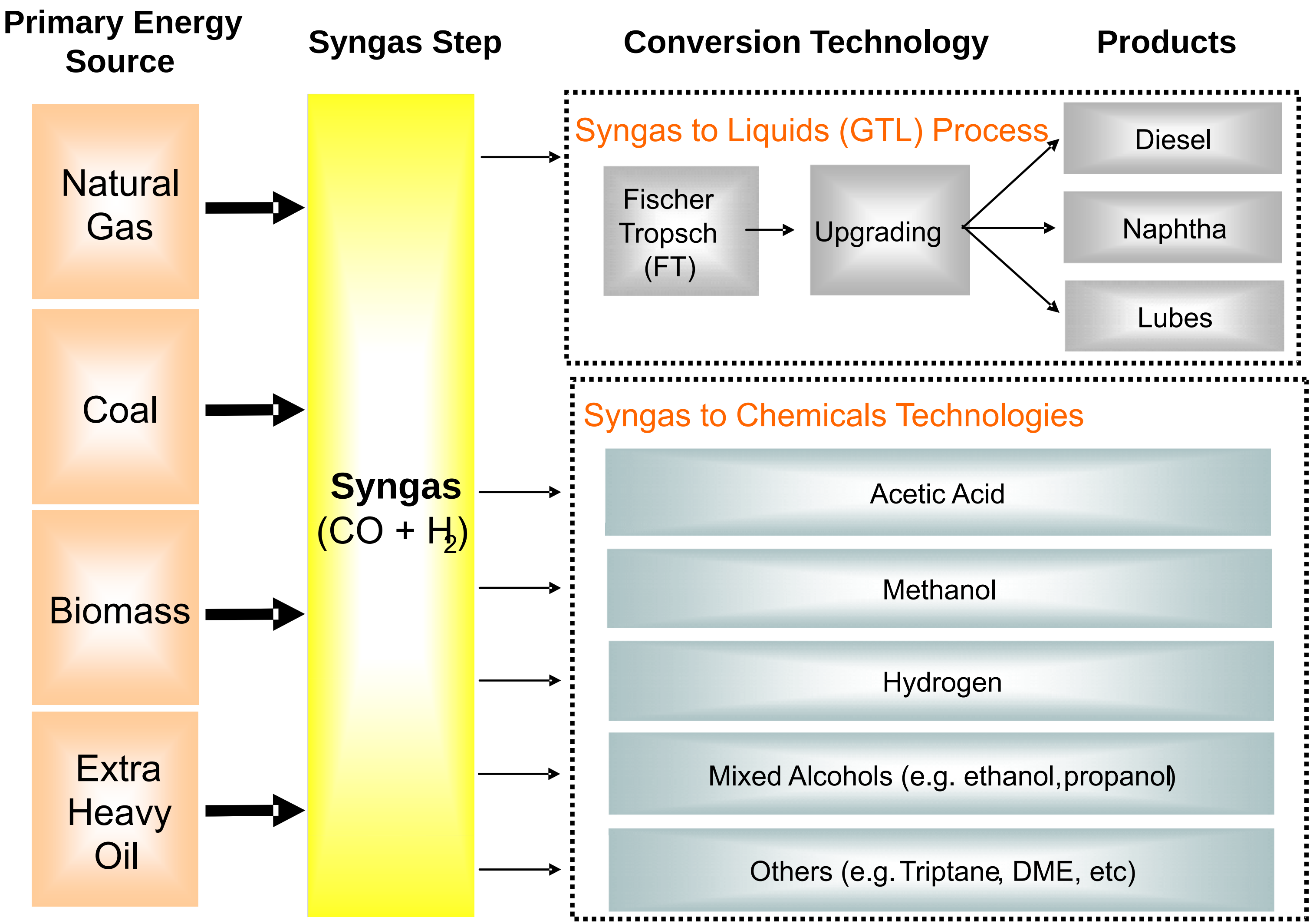
NREL's THERMOCHEMICAL PLATFORM

Major Research Tasks, NREL (FY2011)

1. Gasification
    - Fundamental and applied studies for biomass gasification
2. Pyrolysis
    - Upgrading of pyrolysis oils
    - Catalytic fast pyrolysis
3. SynGas Cleanup
    - Tar reforming catalyst development, catalytic gasification, high temperature H_2S sorbents
4. Fuels Synthesis (mixed alcohols)
    - Catalyst testing and validation
5. Process Integration
    - TC PDU (20 kg/h)
6. Process Analysis and Modeling

Fuels from Syngas

Hydrocarbon fungibility will be a key to success



Primary Energy Source

Syngas Step

Conversion Technology

Products

Natural Gas

Coal

Biomass

Extra Heavy Oil

Syngas ($CO + H_2$)

Syngas to Liquids (GTL) Process

Fischer Tropsch (FT)

Upgrading

Diesel

Naphtha

Lubes

Syngas to Chemicals Technologies

Acetic Acid

Methanol

Hydrogen

Mixed Alcohols (e.g. ethanol, propanol)

Others (e.g. Triptane, DME, etc)

Source: BP

THERMOCHEMICAL PLATFORM: STATE OF TECHNOLOGY

	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	90	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	2000	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 - CO2 free basis (%)	80	80	80	80	80	80	80
Total Alcohol Productivity (g/kg/hr)	300	300	300	300	450	600	600

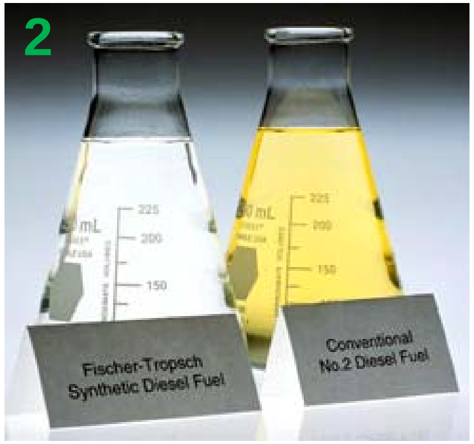
Major Focus 2005-2010
(Single Pass)

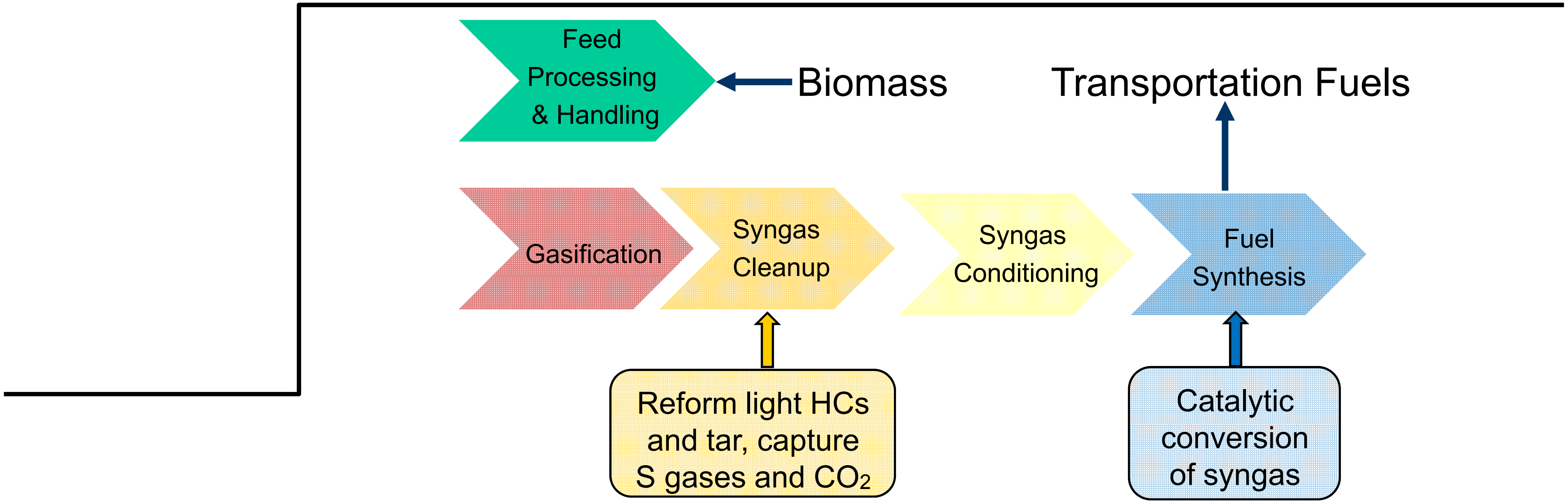
Major Focus 2009-2012

THERMOCHEMICAL CONVERSION: GASIFICATION

Biomass via synthesis gas to fuels

1. Deconstruct biomass all the way to light gases (CO & H_2)
2. Convert syngas to liquid fuels





Feed Processing & Handling

Biomass

Transportation Fuels

Gasification

Syngas Cleanup

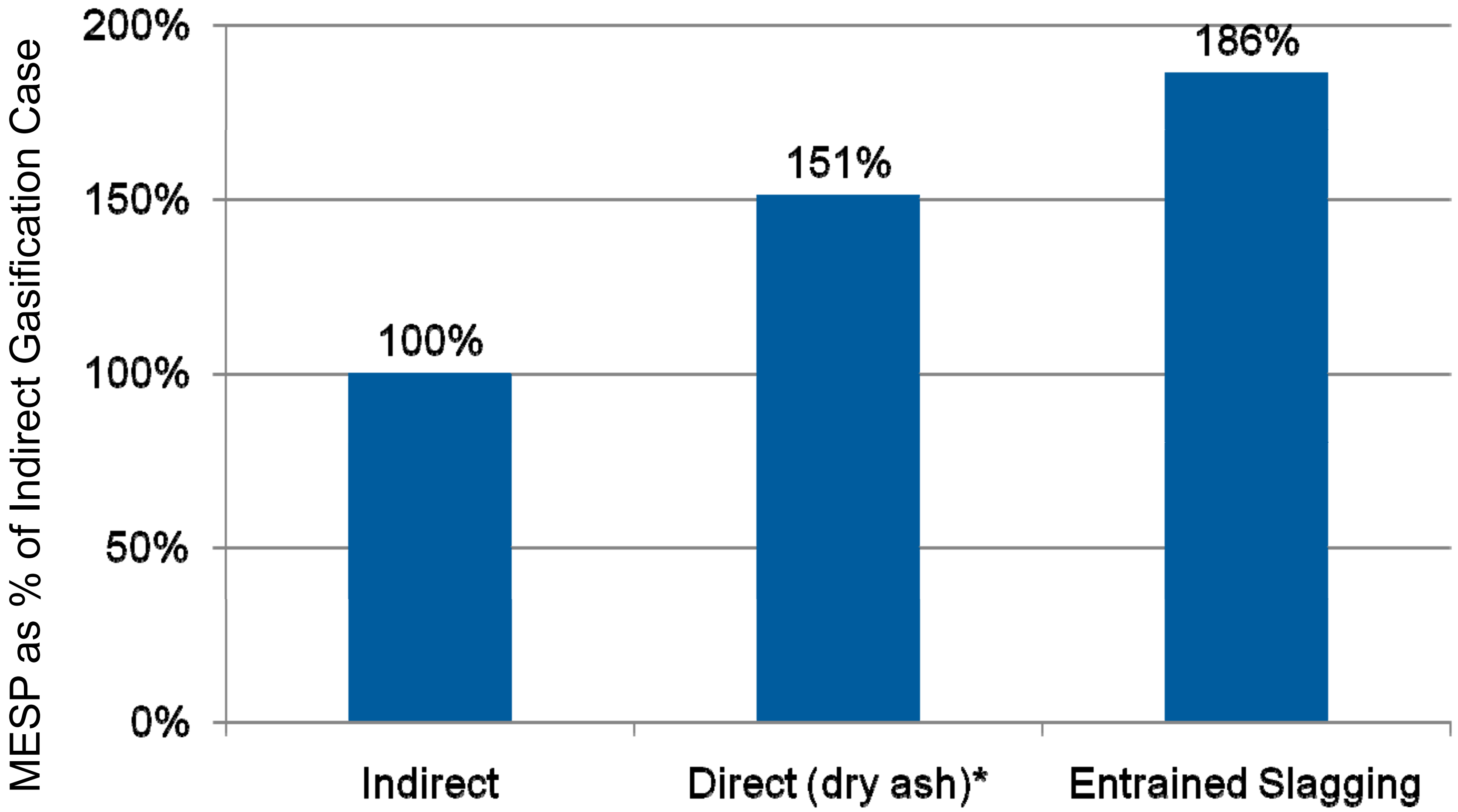
Syngas Conditioning

Fuel Synthesis

Reform light HCs and tar, capture S gases and CO_2

Catalytic conversion of syngas

GASIFIER TYPES FOR FUEL SYNTHESIS



Indirect gasification is one of the lowest cost options

Syngas Composition

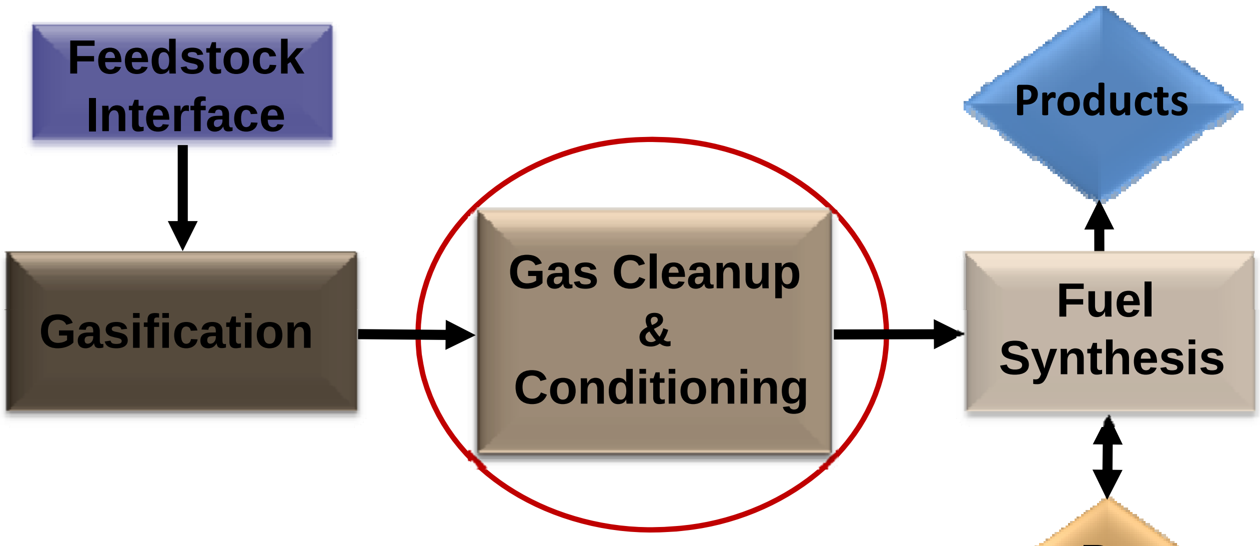
Typical gas compositions of three indirect gasification processes (wood as fuel)

Gas component, dry basis		FICFB (Güssing)	SilvaGas	MILENA (ECN)
Hydrogen	vol%	30-45	20-22	15-20
Carbon monoxide	vol%	20-30	41-44	40-43
Carbon dioxide	vol%	15-25	11-14	10-12
Methane	vol%	8-12	12-16	15-17
C2+ hydrocarbons	vol%	1-3	4-6	5-6
Benzene	vol%	1	1	
Nitrogen	vol%	1-3	2-10	1-4
Ammonia	ppmV	500-1000	500-1000	
H2S	ppmV	50-120	40-100	
Tar	g/mn3	0.5-1.5	40	40
Particles	g/mn3	10-20	~	

Contaminants

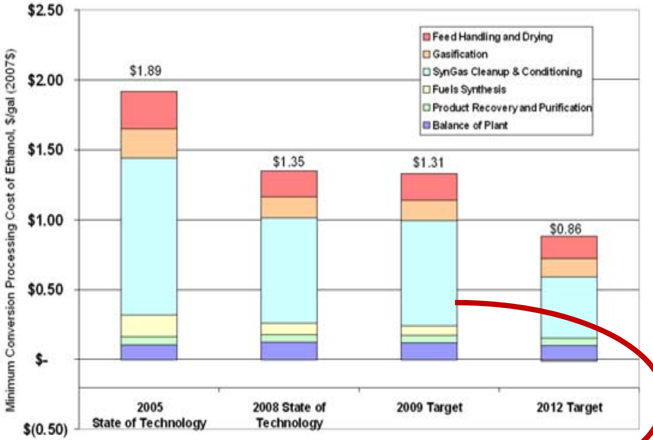
Stergaršek et al. Workshop proceedings Production and Purification of Fuel from Waste and Biomass, October 2004.

Biomass Derived Syngas Cleaning



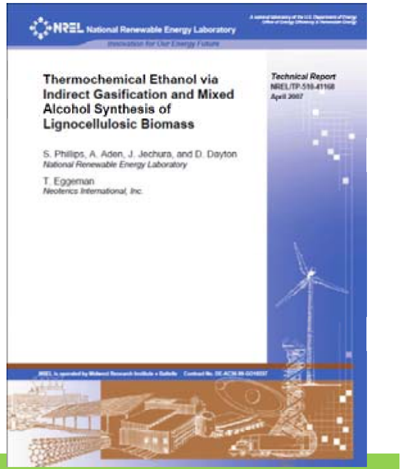
Alcohols
Gasoline
Green
Diesel
FT Liquids

Robust **methane**/tar reforming catalysts
High temperature sulfur sorbents
Integrated syngas cleaning process



Project rationale:
Syngas cleaning significant process cost component

Syngas Cleaning Targets
Methane conversion: 80%
Benzene conversion: 99%
Tars/HC conversion: 99%
Meet $1.57 gal



NREL National Renewable Energy Laboratory

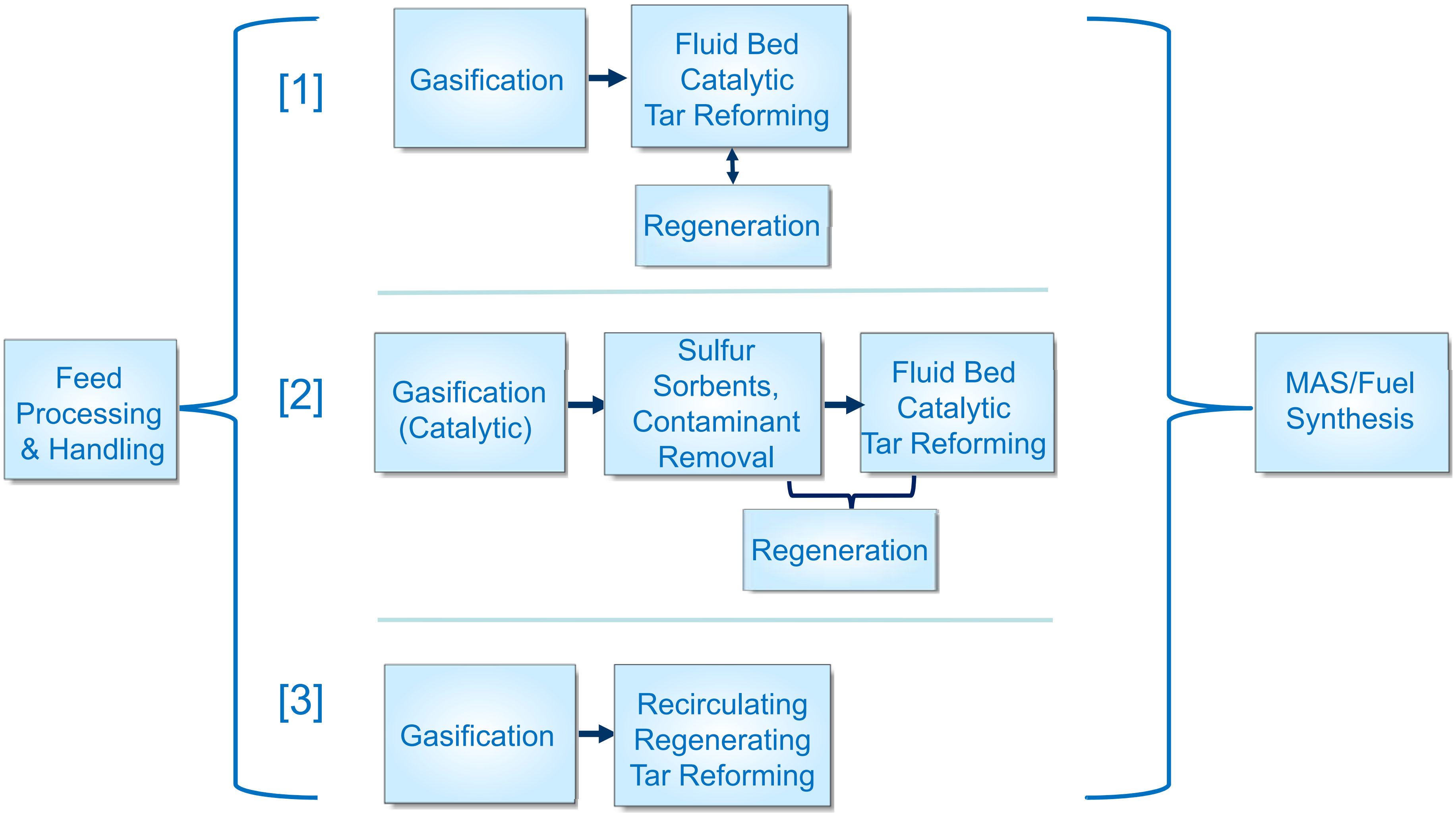
Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass

S. Phillips, A. Aden, J. Jechura, and D. Dayton
National Renewable Energy Laboratory

T. Eggeman
Neoterics International, Inc.

Technical Report
NREL/TP-510-41168
April 2007

Biomass Syngas Cleaning Strategies



Feed Processing & Handling

[1]

Gasification

Fluid Bed Catalytic Tar Reforming

Regeneration

[2]

Gasification (Catalytic)

Sulfur Sorbents, Contaminant Removal

Fluid Bed Catalytic Tar Reforming

Regeneration

[3]

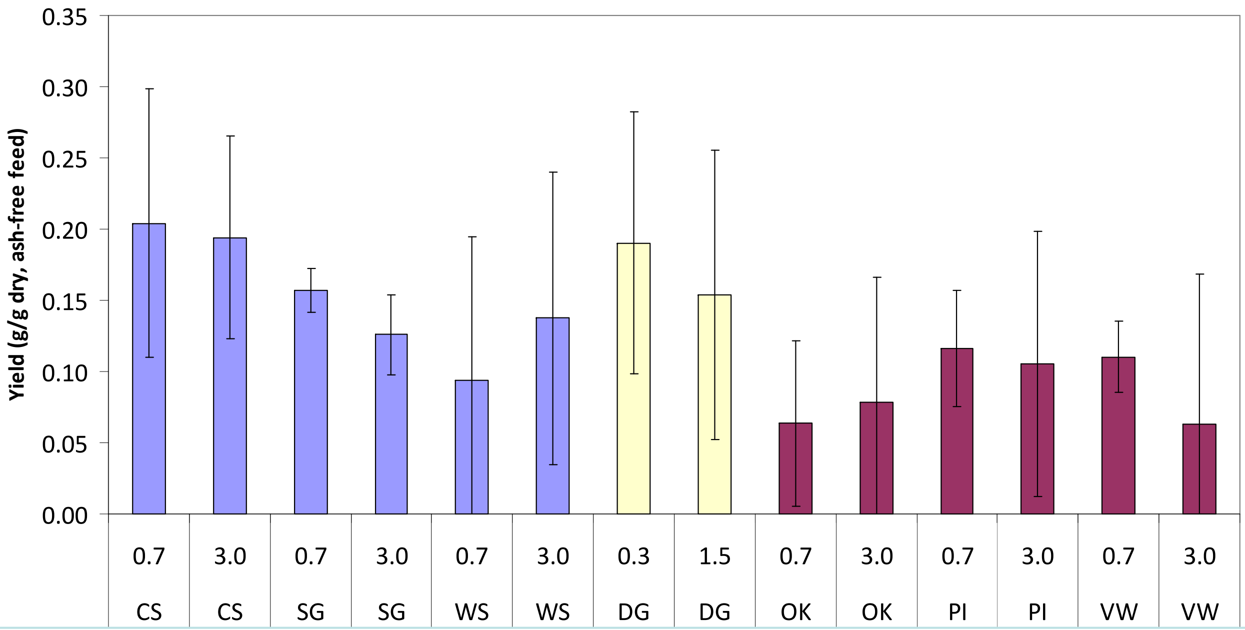
Gasification

Recirculating Regenerating Tar Reforming

MAS/Fuel Synthesis

Routes 1,3: Process Intensification

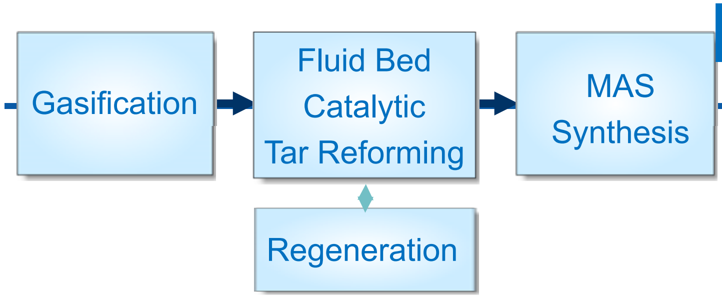
Feedstock Impact on Syngas Composition



- Tars calculated by difference in units of g tar/g dry, ash-free feed

- Results are color-coded by feedstock type (herbaceous, distillers dry grains, and woody)

- Slightly less tars produced from woody feedstocks



Gasification

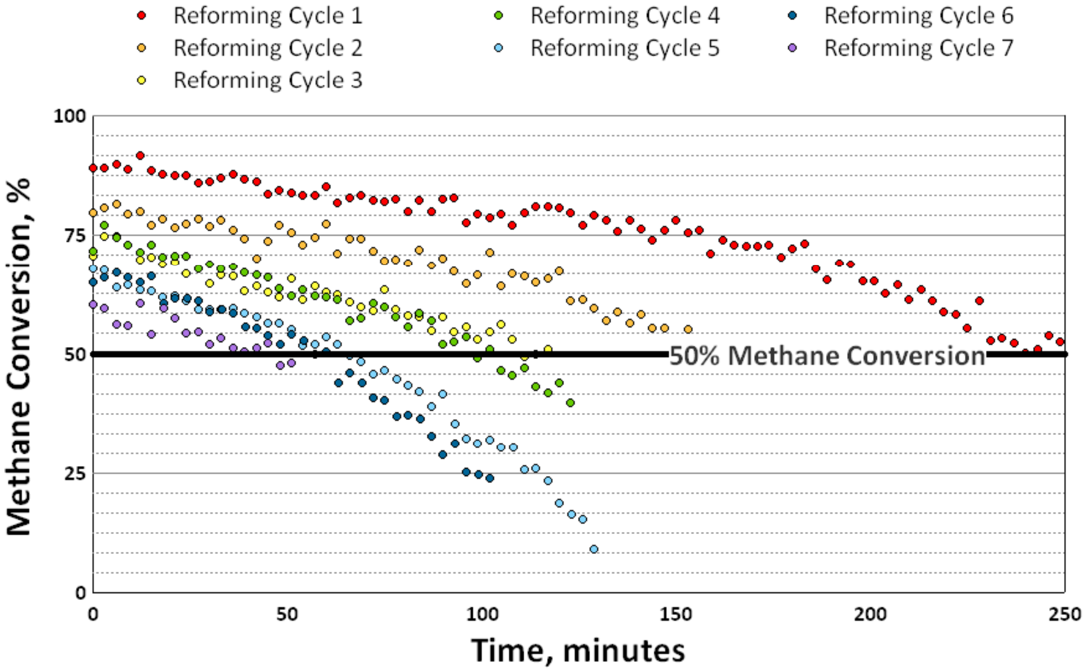
Fluid Bed Catalytic Tar Reforming

MAS Synthesis

Regeneration

FLUID BED TAR REFORMING

Challenge: *Continuously reform tars and methane in the presence of H_2S and other contaminants*

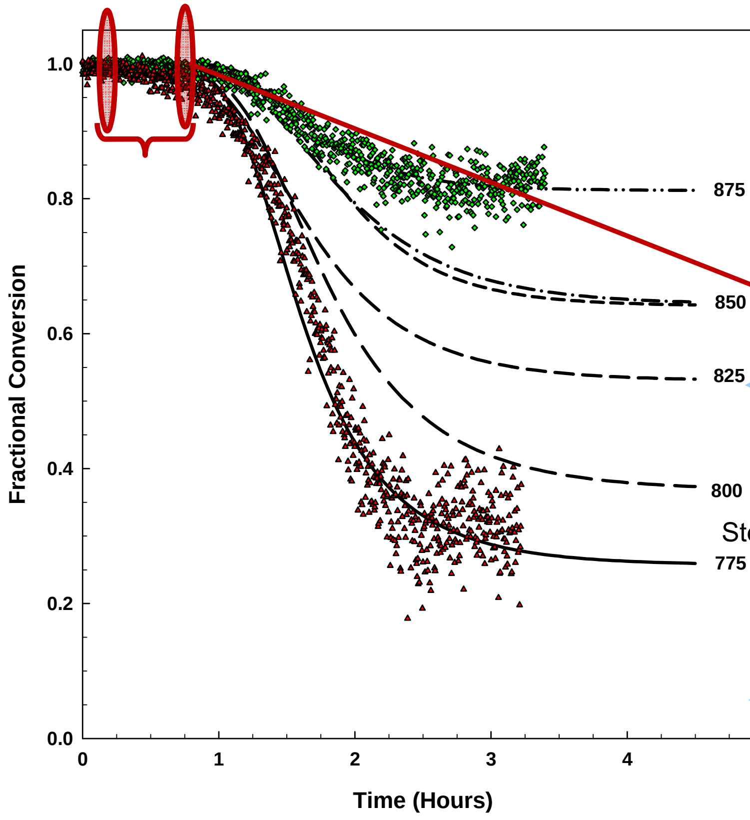


Indirect, two-stage steam gasification
- 8” FBR, 700-850° C
- Crushed oak pellets (15 kg/h)
- 1:1 steam-to-biomass

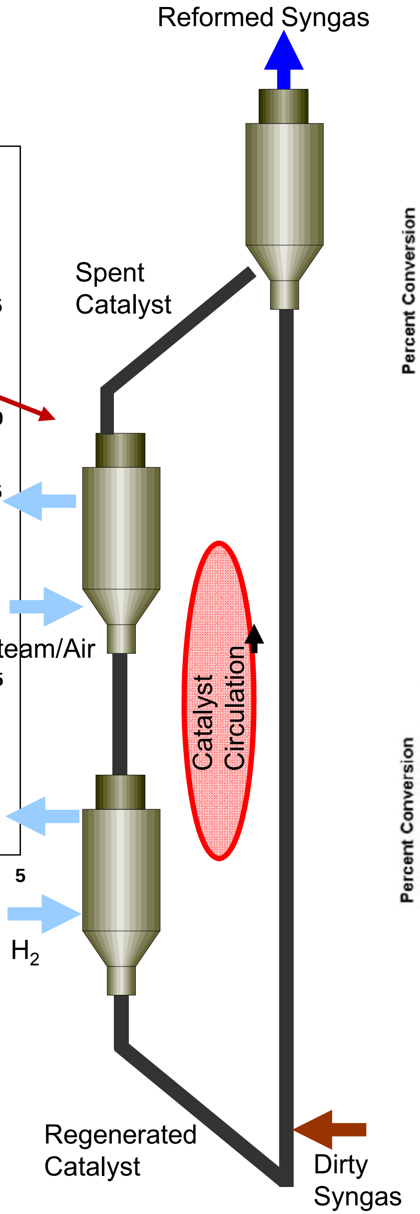
Steam reformer
- 14” FBR
- 850-900° C
- 60 kg catalyst
- GHSV ~5000 h^{-1}

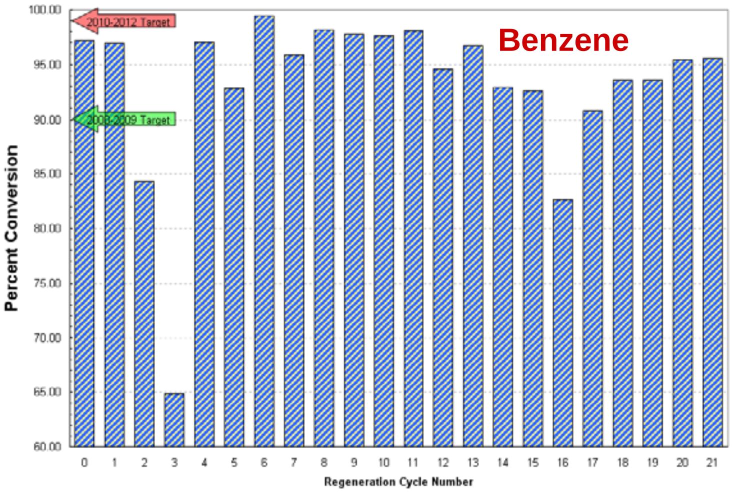
$Ni-K-Mg/Al_2O_3$ fluidizable catalyst
- Deactivates in H_2S
- Loses CH_4 reforming
- Maintains tar, benzene conversion

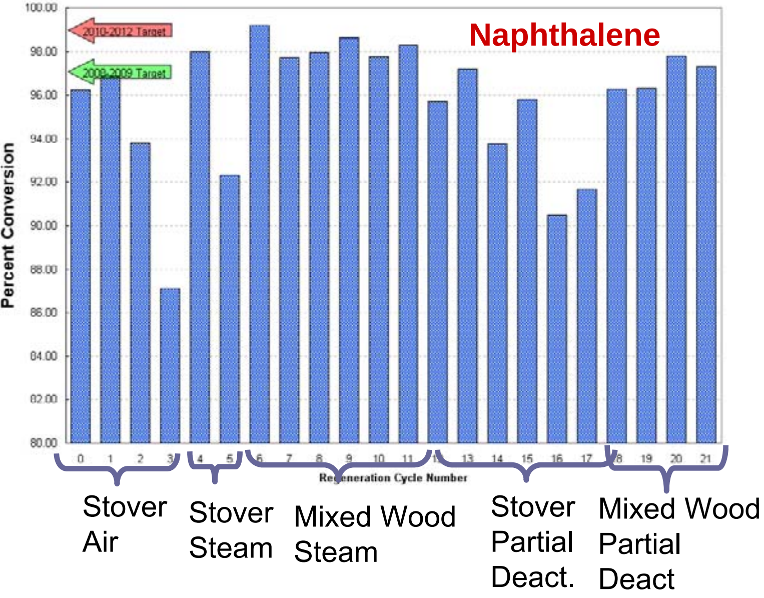
FLUIDIZED S TOLERANT REFORMING CATALYST



Alkali-promoted Ni/Al_2O_3







Syngas Cleanup and Conditioning Chemistry

Reaction chemistry

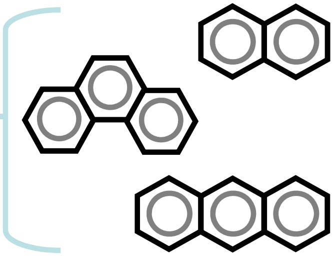
Reforming: $CxHyOz + H2O(g) \longrightarrow H2 + xCO$

Water gas shift: $H2O + CO \longrightarrow CO2 + H2$

Gasification: $C + H2O(g) \longrightarrow COx + H2$

Process conditions

- 800-950°C
- Steam
- Tars
- Fluid catalyst bed
- S, Cl species
- Syngas (CH4, CO, H2 ,CO2)

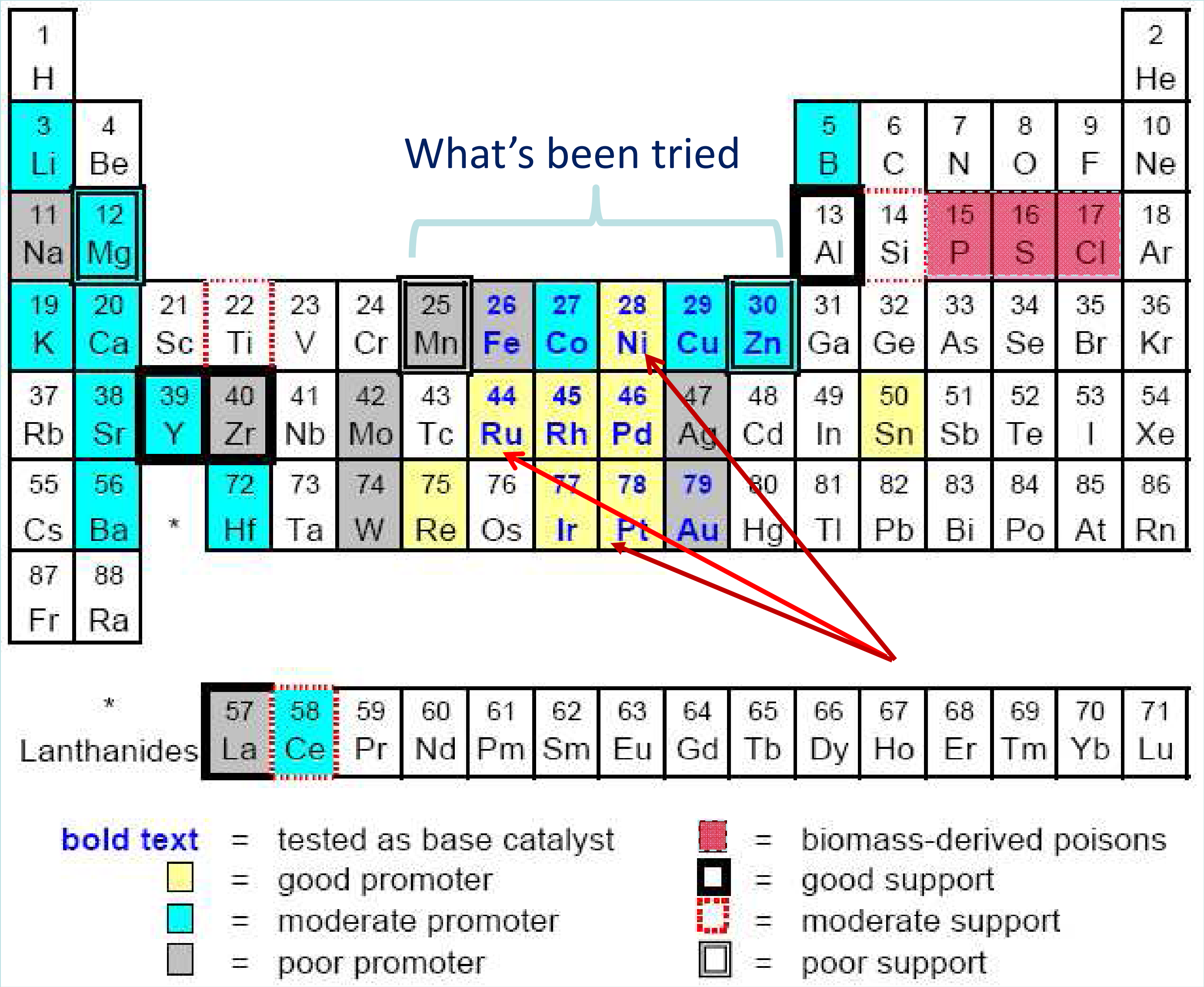


Single composite catalyst facilitating complex and simultaneous reactions

Tar Reforming Catalyst Challenges

1) **High activity**
   - **Short contact times**
2) **Sulfur tolerance**
3) **Efficient regeneration**
4) **Attrition resistance**
5) **Technical Targets**
   - **Total tars conversion > 99%**
   - **Benzene conversion > 90%**
   - **Methane conversion > 90%**

Reforming Catalyst Development



bold text = tested as base catalyst
🟨 = good promoter
🟦 = moderate promoter
⬜ = poor promoter
🟥 = biomass-derived poisons
■ = good support
⬚ = moderate support
☐ = poor support

Increasing cost ↓

Yung, Jablonski, Magrini. *Energy and Fuels*, 2009 (23), 1874-1887.

Catalyst Design and Evaluation: C_2H_4 Reforming

Catalyst	wt% NiO	wt% MgO	wt% K2O	Support	Ni/Mg	Steam Ref	+ 20 ppm H_2S	After regen
Cat. 32a	6.1	2.4	3.9	Al2O3	2	97	13	98
Cat. 34a	3			Al2O3		30	20	18
Cat. 34b	6			Al2O3		19	19	48
Cat. 34c	9			Al2O3		52	70	95
Cat. 34d	3	5.5	0.08	Al2O3	0.5	37	37	37
Cat. 34e	6	1.8	0.17	Al2O3	3.3	96	43	100
Cat. 34f	6	3.6	0.17	Al2O3	1.7	91	37	69
Cat. 34g	3	1.8	0.08	Al2O3	1.7	80	30	87
Cat. 34h	3	3.6	0.08	Al2O3	0.8	82	21	82
Cat. 34i	3	5.5	0.08	Al2O3	0.5	78	16	76
Cat. 34j	6	1.8	0.16	Al2O3	3.3	94	55	30
Cat. 34k	6	3.6	0.16	Al2O3	1.7	86	58	95
Cat. 34l	6	5.5	0.16	Al2O3	1.1	88	38	92
Cat. 34m	9	1.8	0.24	Al2O3	5	98	73	100
Cat. 34n	9	3.6	0.24	Al2O3	2.5	95	49	NA
Cat. 34o	9	5.5	0.24	Al2O3	1.6	93	53	100
Cat. 35a	3	3	0.09	Al2O32	1	79	12	79
Cat. 35b	3	3	0.08	Zr-Al2O3	1	68	20	71
Cat. 35c	1.5	1.5	0.04	Zr-Ceria	1	61	8	60
Cat. 35d	3	3	0.08	Ce-Zr- Al2O3	1	82	16	82

Catalyst and Sorbent Development Approach

Reforming catalyst and sulfur sorbent development and testing with model syngas

Down select promising catalysts and sorbents that meet cleaning and cost * targets

Evaluate catalyst sorbent combinations with simulated process conditions

Down select syngas cleaning process that meets targets for 2012 demonstration

***2012 cost target: modeled MESP of $1.57/gal**

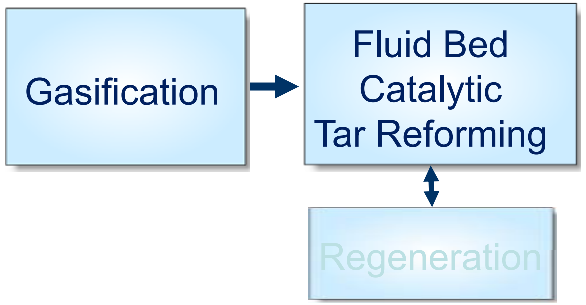
- Evaluation with raw syngas is key to determining catalyst and sorbent performance
- Lab developed and emerging industrial catalysts rapidly screened with **decision point** after initial screening
- Improvements incorporated into process model
- Best process demonstrated at pilot scale in 2012

Reforming Catalyst Regeneration

Challenge:
Biomass syngas contains contaminants (H2S, HCl) that deactivate methane reforming catalysts

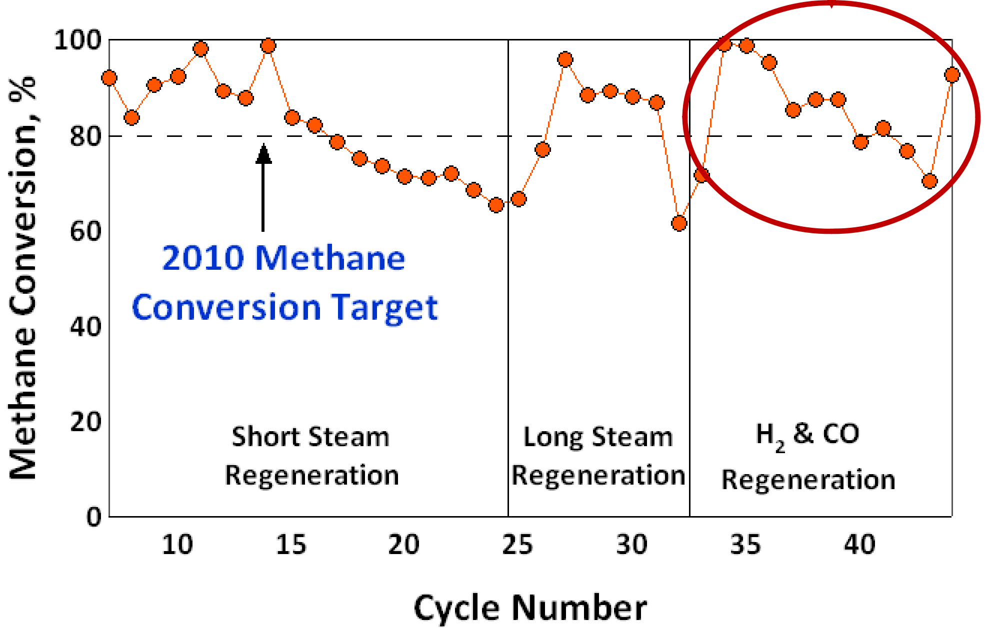
General Approach 1:

- Crack tars/reform methane with contaminants present
  - ***Frequent/continuous regeneration of Ni-based reforming catalysts using optimized regeneration process:***



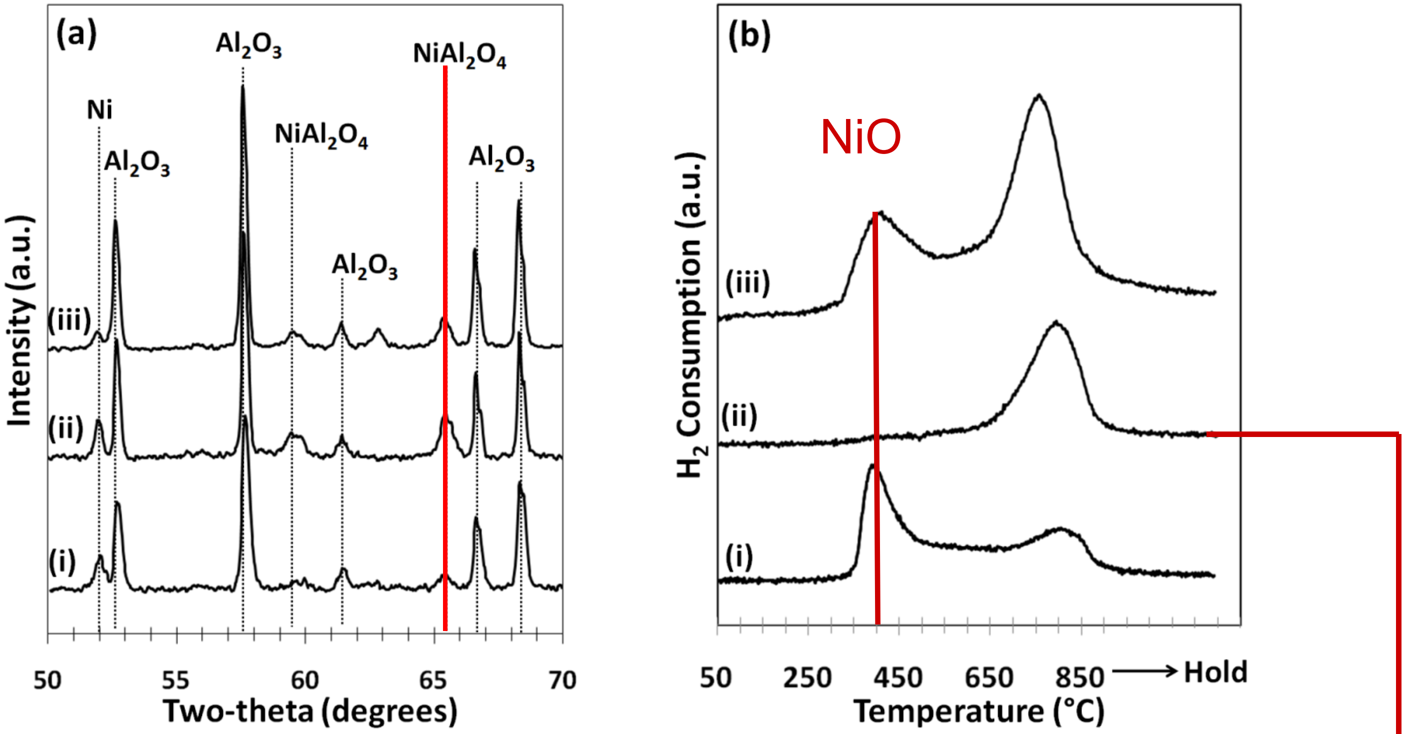
	Low	Mid	High
H_2	H_2:CO = 1.6	H_2:CO = 3.1	H_2:CO = 4.6
H_2O	S:C = 1.0	S:C = 3.9	S:C = 10
CO_2	CO_2:CO = 1.0	CO_2:CO = 1.6	CO_2:CO = 2.1

Stage 3 regeneration experiment design values and levels



Achieved tar reforming efficiency of ≥ 80% methane, 99% benzene, and 99% heavy tars through improved catalyst composition and regeneration processes

Understanding Catalyst Deactivation and Regeneration



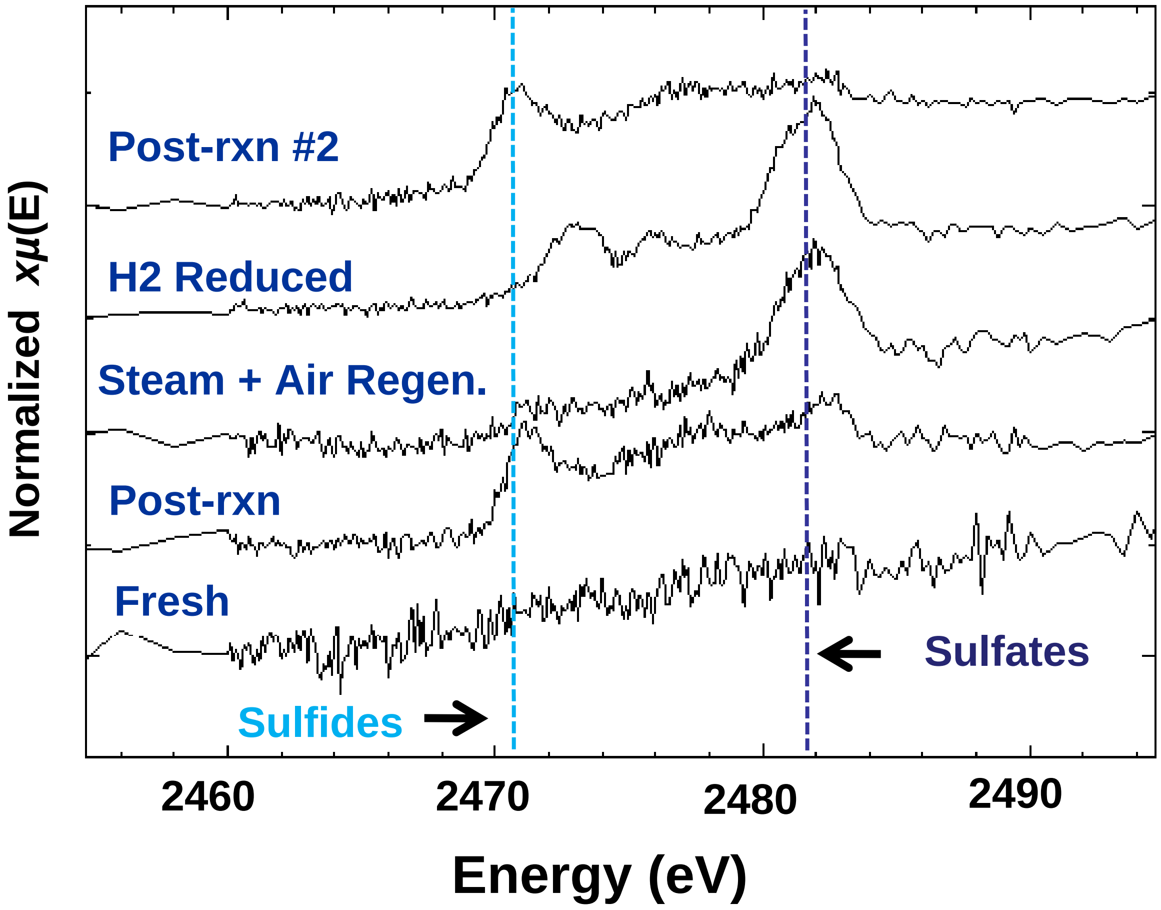
a) XRD patterns and (b) H2 TPR profiles of post-reaction catalysts tested in:

(i) fixed-bed reactor, bench scale conditions with model syngas
(ii) pilot-plant fluidized bed reactor with real syngas
(iii) pilot-plant recirculating/regenerating reactor using model syngas

Catalyst used with model syngas has more free Ni available for further reforming

What in raw syngas causes this? – current and future work

Effect of Catalyst Regeneration on Sulfur (S-XANES)



Direct observation of sulfur species after reaction and regeneration steps

Transformation of sulfides to sulfates (not fully removed from surface)

Guided protocol for improved regeneration (time, temperature, environment)

2010 E MS: Use of EXAFS and XANES to investigate the fate of nickel and biomass inorganic contaminants on catalysts

Effect of treatment on sulfur chemistry provides understanding and improvement of regeneration processes

Stanford Synchrotron
Radiation Lightsource

Reforming Catalyst Improvement

Fundamental Challenge:

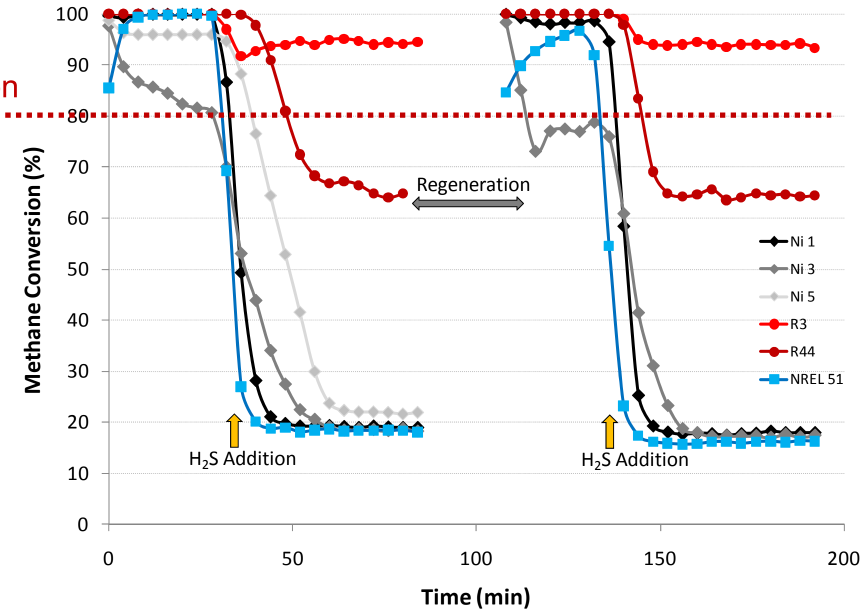
Biomass syngas contains contaminants (H2S, HCl) that deactivate methane reforming catalysts

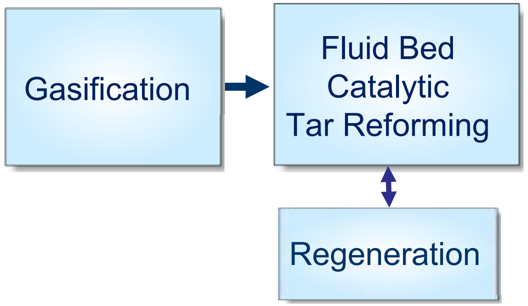
Approach 1:

Crack tars/reform methane with contaminants present

- ***Develop contaminant resistant catalysts that can be regenerated using:***

2010 Target:
80% CH4 conversion





Achieved tar reforming efficiency of ≥ 80% methane, 99% benzene, and 99% heavy tars through improved catalyst composition and regeneration processes

PGM/alumina outperforms NREL and Johnson Matthey Ni/alumina reforming catalysts

PGM sulfur tolerant in 60 ppm H2S and regenerable

Cycled experiments show coupled reforming and regeneration reproducible

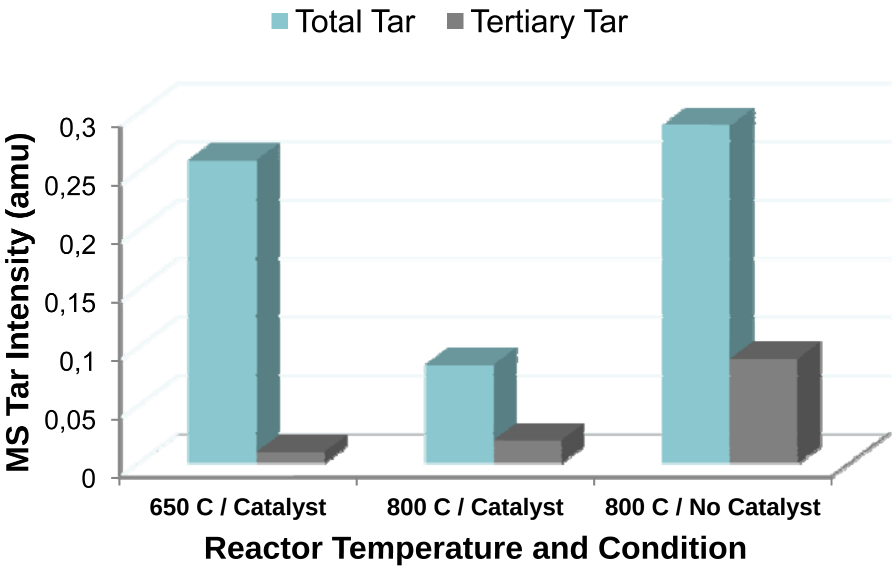
Cost to be determined on process impact

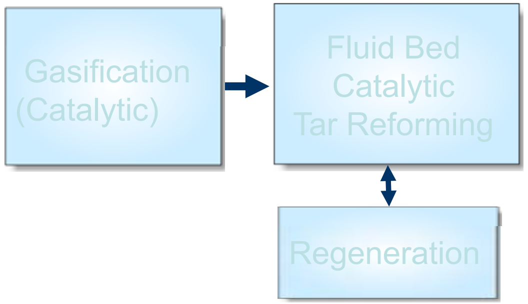
Catalytic Gasification

Fundamental Challenge:
Biomass syngas contains contaminants (H2S, HCl) that deactivate tar cracking/methane reforming catalysts

General Approach 2:

- Reduce contaminants before catalytic reforming
  - ***Develop in bed gasification catalysts to reduce/eliminate tars as they form using:***





Gasification (Catalytic)

Fluid Bed Catalytic Tar Reforming

Regeneration

Ni impregnated olivine gasification catalyst prepared in house

Total tar in the gasification product gas measured by MBMS (sum 50-450 amu)

10% less tar forms at 650°C with catalyst than at 800°C without catalyst

70% less tar forms at 800°C with catalyst than without

Less tar reduces load on the reforming catalyst

Catalytic Gasification

Fundamental Challenge:
Biomass syngas contains contaminants (H2S, HCl) that deactivate tar cracking/methane reforming catalysts

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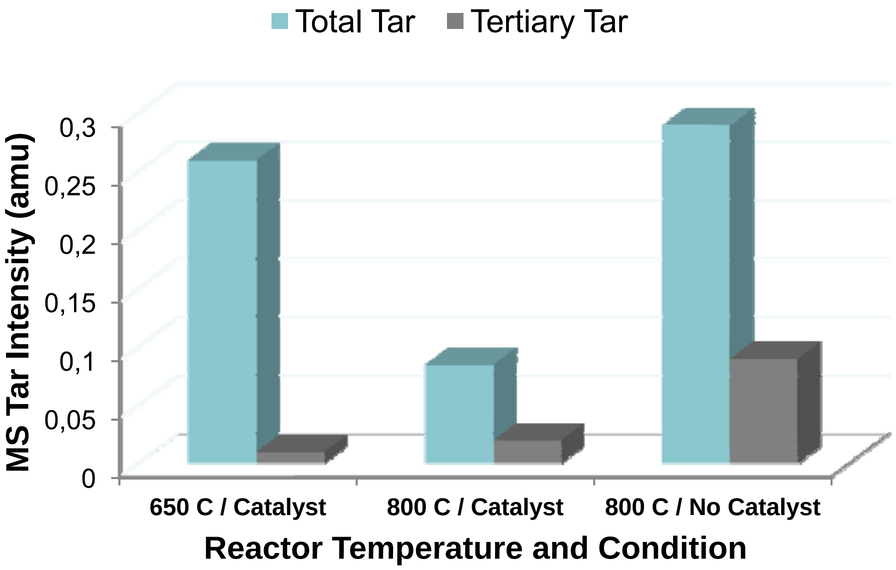
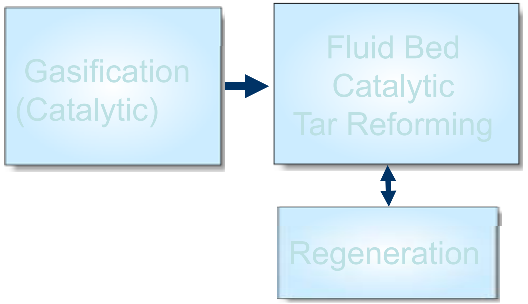
  - ***Develop in bed gasification catalysts to reduce/eliminate tars as they form using:***





Ni impregnated olivine gasification catalyst prepared in house

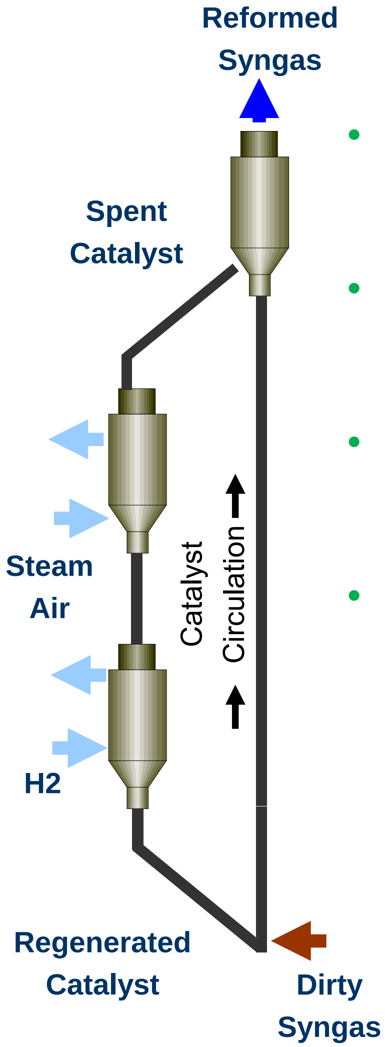
Total tar in the gasification product gas measured by MBMS (sum 50-450 amu)

10% less tar forms at 650°C with catalyst than at 800°C without catalyst

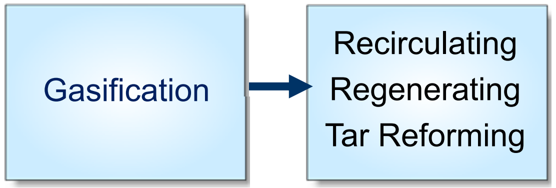
70% less tar forms at 800°C with catalyst than without

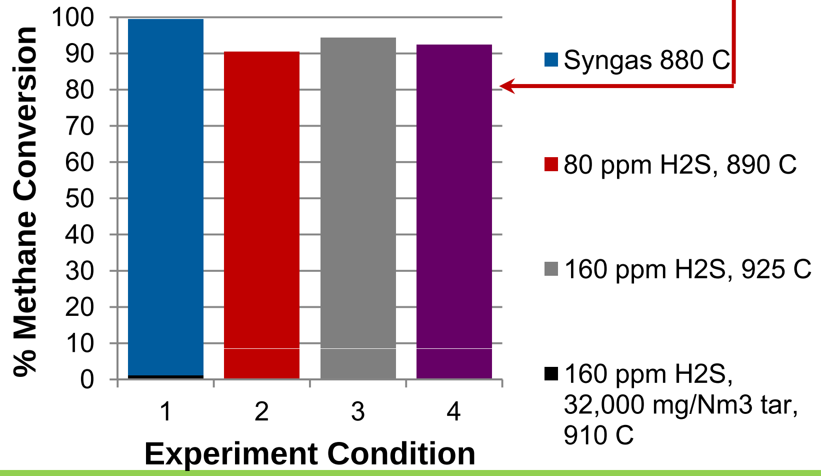
Less tar reduces load on the reforming catalyst

SYNGAS CLEANUP: CONTINUOUS REFORMING/REGENERATION



- Hypothesis: Ni-alumina reforming catalyst is regenerable after reaction with H_2S in raw syngas
- Regenerability extent determined by contact time and process conditions (gas compositions, temperature)
- Industrial collaborator (Rentech) evaluated NREL catalyst for 100 h of tar reforming simulated syngas containing H_2S and SO_2
- Methane conversion maintained at > 92% under recirculating regenerating (R^2) conditions
- Economic impact: process intensification





FUEL SYNTHESIS: MAS CATALYST STRATEGY

Construction and operation of advanced test reactor systems

- *Built-in capability for a variety of catalysts (vision beyond 2012)*
- *Capability to feed syngas directly from the TCPDU*
- *Allows around-the clock unmanned operation for faster throughput/catalyst lifetime studies*

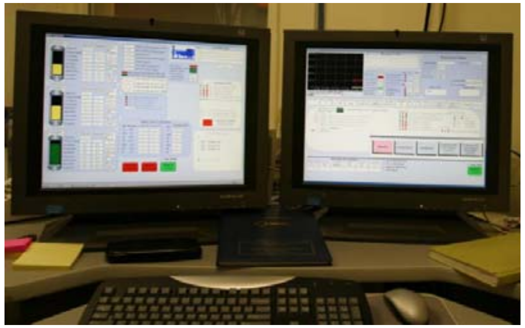
Improved MAS Catalysts in support of 2012 cost target

- *Test improvements to Dow catalyst and continue to optimize conditions through collaborative research under Dow CRADA*
- *Work with PNNL to test rhodium-based catalyst with TCPDU derived syngas and optimize run parameters*
- *Targeting higher ethanol selectivity and ethanol productivity*

stirred tank reactor system ↓

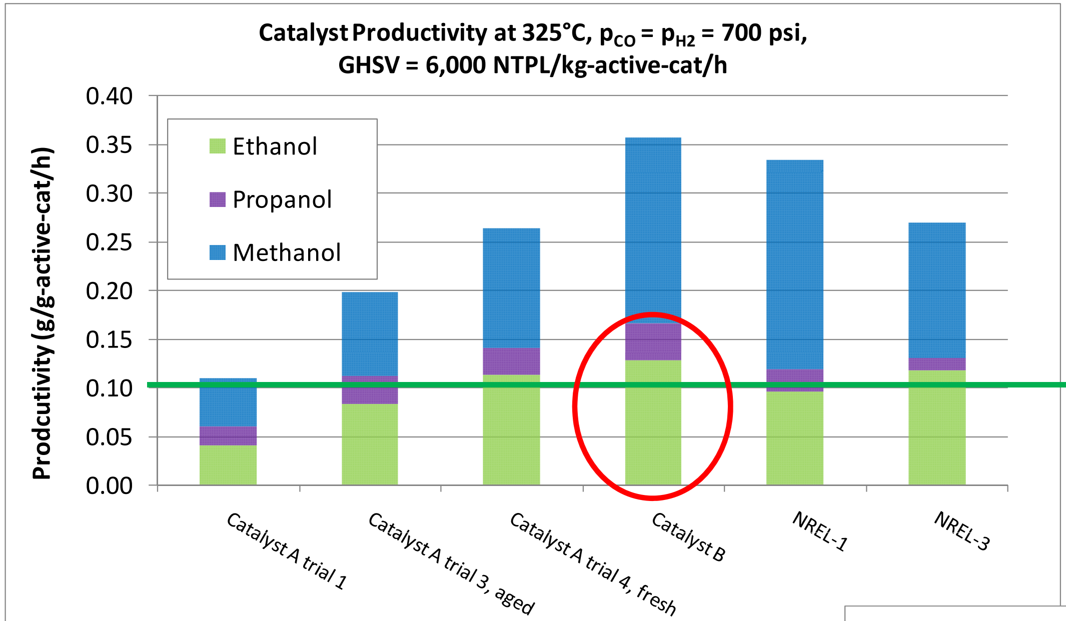
gas compression system →

control station ↓



← mixed gas storage and delivery

Sulfide Catalyst Improvements

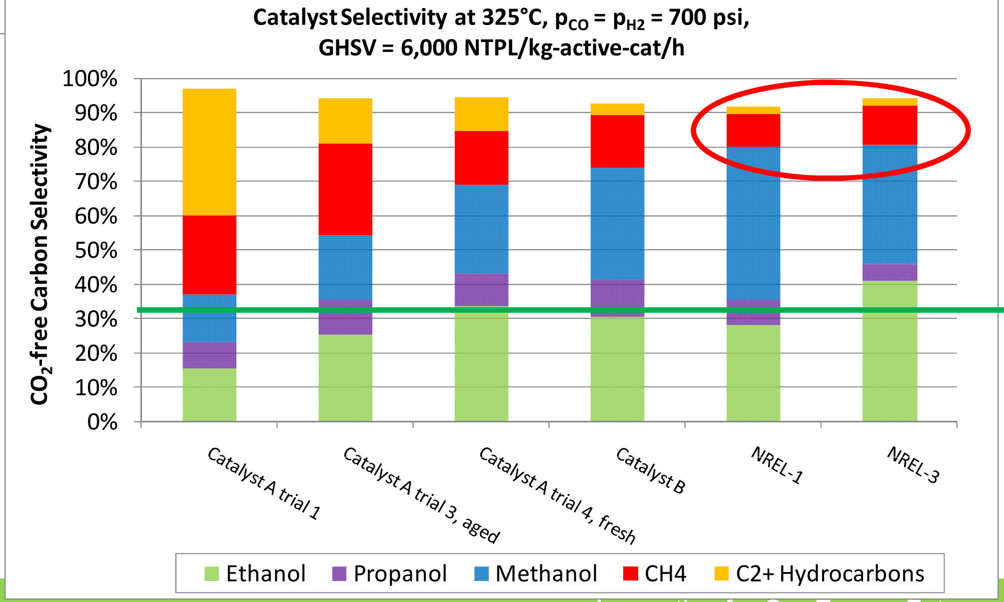


CoMoSx-type catalysts tested in FBR

- catalysts A,B are industrial materials
- other catalyst is NREL formulation

State-of-art material

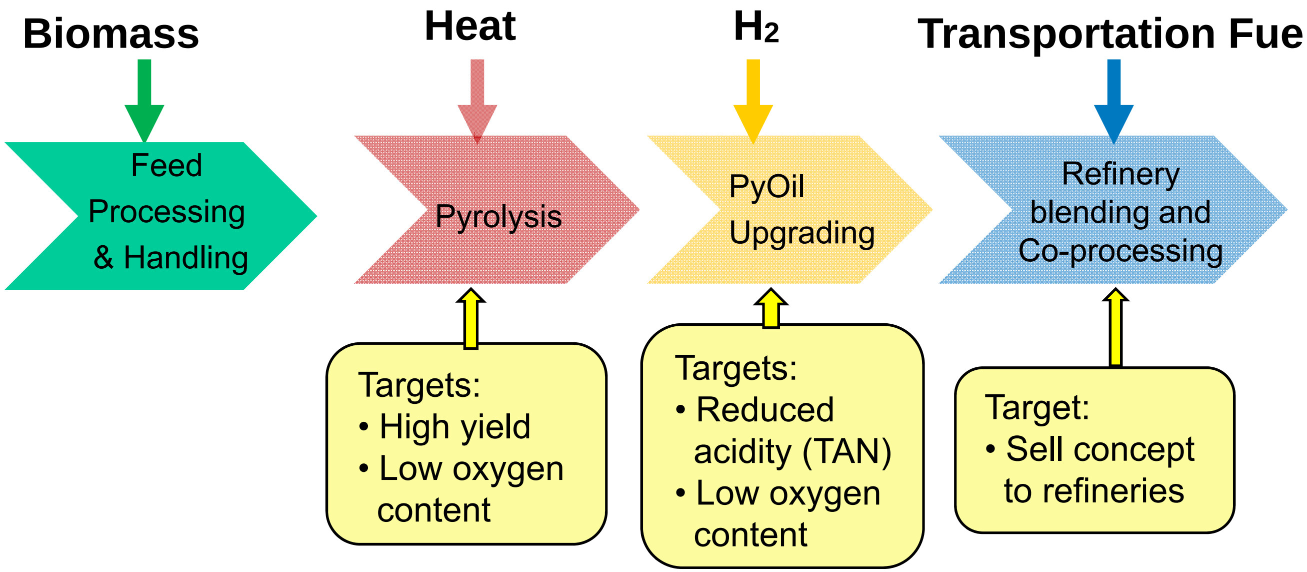
Observed significant improvements in ethanol productivity, hydrocarbon selectivity (circled in red)



THERMOCHEMICAL CONVERSION: PYROLYSIS

Biomass via pyrolysis oils to fuels

3. Partially deconstruct biomass to liquids
4. Refine liquids to fuels



Biomass → Feed Processing & Handling

Heat → Pyrolysis

H_2 → PyOil Upgrading

Transportation Fuels → Refinery blending and Co-processing

Targets:
- High yield
- Low oxygen content

Targets:
- Reduced acidity (TAN)
- Low oxygen content

Target:
- Sell concept to refineries

CREATING REFINERY READY PYROLYSIS OIL

Production and Processing of Crude Pyrolysis Oil

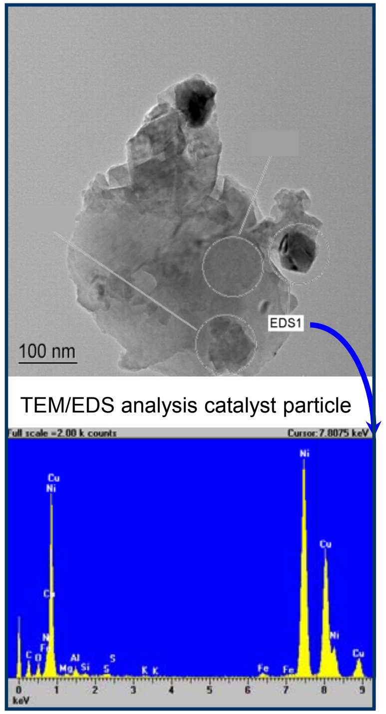
- Catalytic pyrolysis
- Mild hydrotreating for deoxygenation and TAN reduction
- Evaluate compatibility with refinery feedstocks and intermediate streams
  - *composition, properties, miscibility, stability, distillability*
  - *testing of fluids in micro-units that mimic refinery unit operations*

NREL and PNNL are working together and with other partners to facilitate commercialization of pyrolysis for transportation fuels.

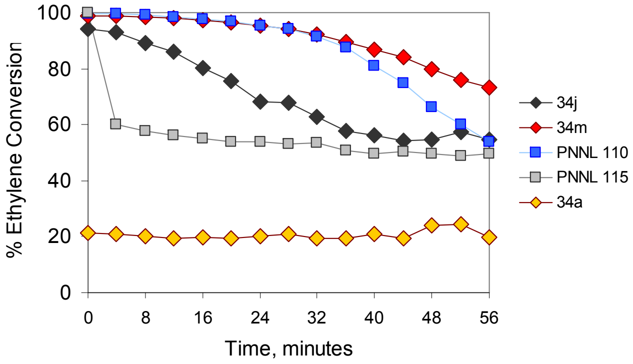
Biomass Catalyst Characterization Laboratory

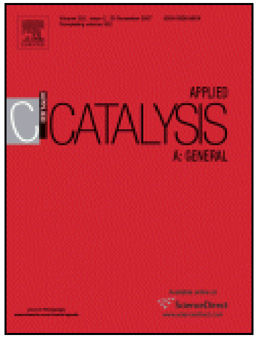
Comprehensive Solids/Liquids Analysis

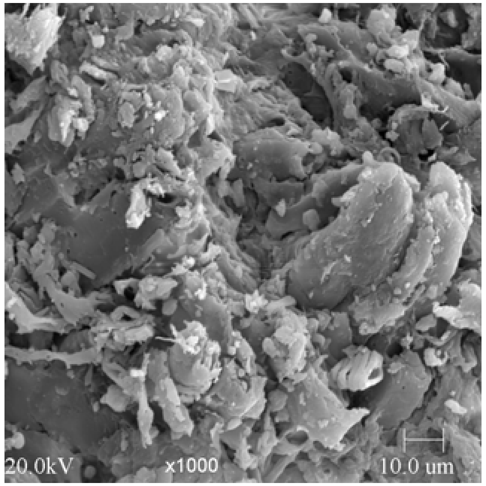
BCCL Instruments	Measures
TGA/DSC/FTIR	Thermal behavior/gas analysis
TGA	Thermal behavior
TPD/MS	Thermal desorption/gas analysis
Porosimeter/pycnometer	Porosity/distribution
Surface area analyzer	Surface area
ICP, XRF	Elemental analysis
Particle Sizer	Particle size/distribution
LECO CHNS, TGA	C, H, N, S, proximate analysis
2D GCMC	Chemical composition (oils)
GC/FID	Fuel composition
XRD	Crystal structure
UV photometer	Gas analysis
Py probe GCMS	Catalytic pyrolysis
FTIR	Gas analysis
SEM/EDS	Surface analysis/composition
Microactivity test systems	Catalyst performance



TEM/EDS analysis catalyst particle







NBC’s Thermochemical User Facility (TCUF)

Simulates thermochemical conversion processes

- Gasification
- Pyrolysis
- Combustion (de-emphasized)

Fully automated 0.5 ton/day biomass conversion

Large scale tar cracking & reforming reactor

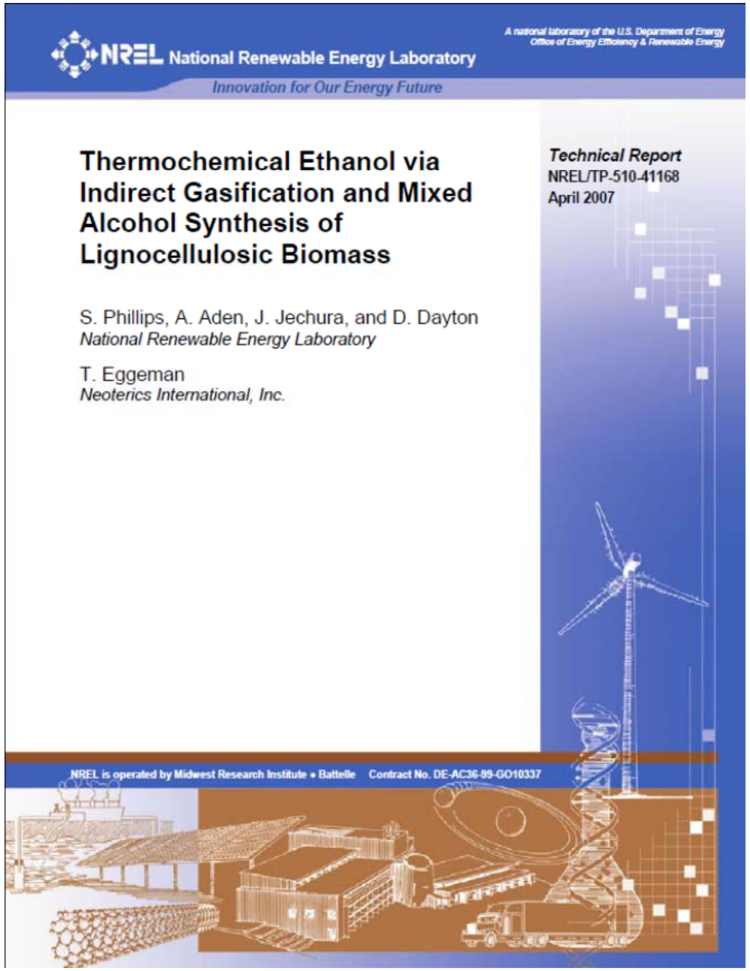
Close-coupled biomass conversion with testing of downstream processes

- 0.1 kg/h to 20 kg/h downstream reactors
- upgrading/conversion research

BIOREFINERY PROCESS ANALYSIS

Design Report

- Mass and energy balances using Aspen Plus
- Discounted cash flow rate of return analysis (DCFROR)
- Calculate minimum product selling price to meet specified IRR (10%)
- Sensitivity Analysis
- Process improvements evaluated yearly



NREL National Renewable Energy Laboratory

Innovation for Our Energy Future

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass

S. Phillips, A. Aden, J. Jechura, and D. Dayton
National Renewable Energy Laboratory

T. Eggeman
Neoterics International, Inc.

Technical Report
NREL/TP-510-41168
April 2007

NREL is operated by Midwest Research Institute • Battelle Contract No. DE-AC36-99-GO10337

NABC National Advanced Biofuels Consortium

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.

ARRA Funded: - 3 year effort

- DOE Funding $33.8M
- Cost Share $12.5M

Total $46.3M

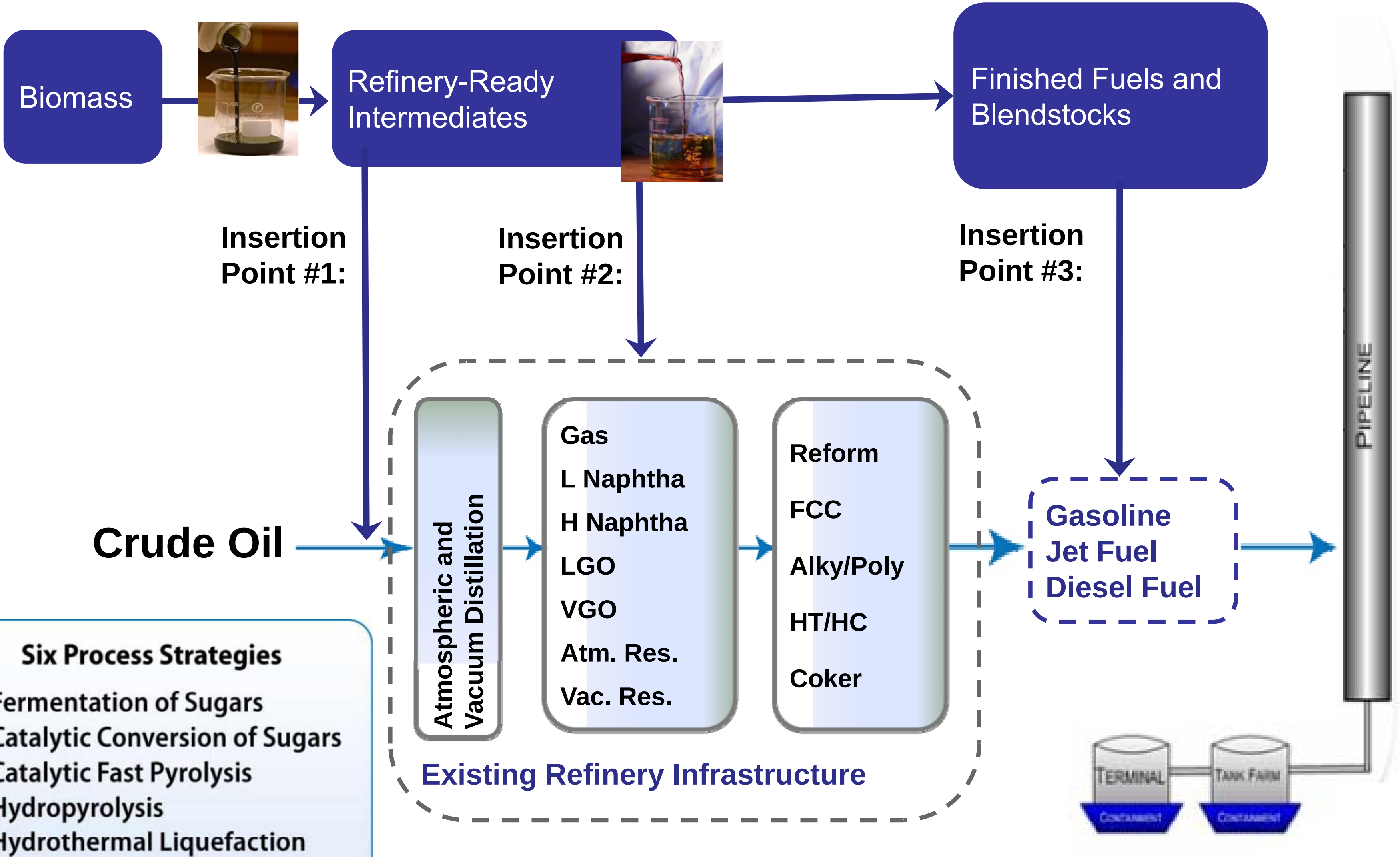
Consortium Leads

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
Virent Energy Systems
Washington State University

NABC: INFRASTRUCTURE COMPATIBILITY STRATEGY



Biomass

Refinery-Ready Intermediates

Finished Fuels and Blendstocks

Insertion Point #1:

Insertion Point #2:

Insertion Point #3:

Crude Oil

Atmospheric and Vacuum Distillation

Gas
L Naphtha
H Naphtha
LGO
VGO
Atm. Res.
Vac. Res.

Reform
FCC
Alky/Poly
HT/HC
Coker

Existing Refinery Infrastructure

Gasoline
Jet Fuel
Diesel Fuel

Six Process Strategies

1) Fermentation of Sugars
2) Catalytic Conversion of Sugars
3) Catalytic Fast Pyrolysis
4) Hydropyrolysis
5) Hydrothermal Liquefaction
6) Syngas to Distillates

Major DOE Biofuels Project Locations

✦ **Four Commercial-Scale Biorefinergy Projects: up to $305 million**

★ **Nine Small-Scale (10%) Biorefinery Projects: up to $240 million (first round)**

★ **Three Bioenergy Centers: up to $405 million**

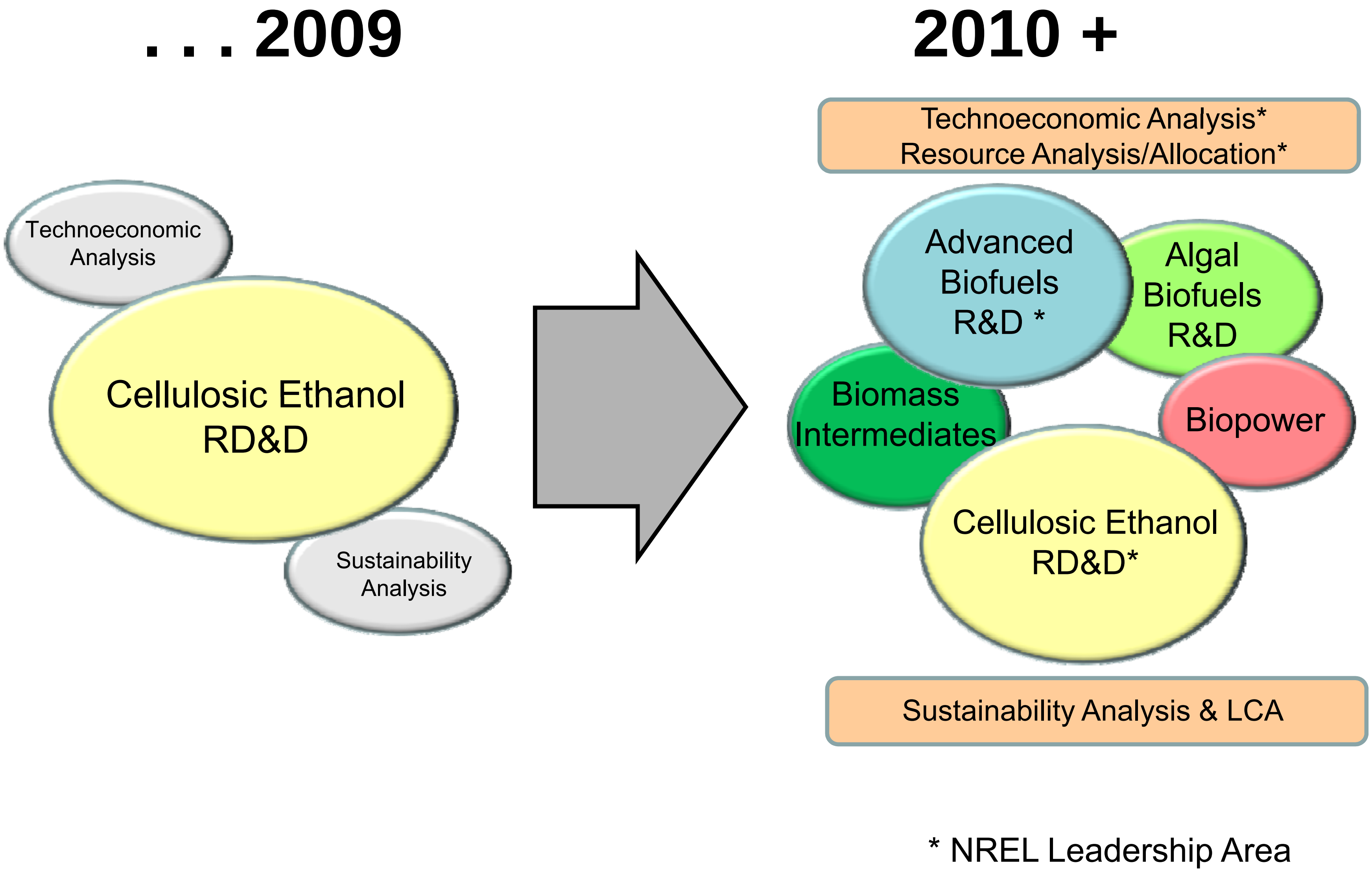
✹ **Four Thermochemical Biofuels Projects: up to $7.7 million**

✺ **Four Improved Enzyme Projects: up to $33.8 million**

✦ **Five Projects for Advanced Ethanol Conversion Organisms: up to $23 million**

Regional Partnerships
South Dakota State Univ., Brookings, SD
Cornell University, Ithaca, NY
Univ. of Tennessee, Knoxville, TN
Oklahoma State Univ., Stillwater, OK
Oregon State Univ., Corvallis, OR

MANAGNG THE TRANSITION IN SCOPE



* NREL Leadership Area

Questions?