BioEnergy

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&

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STONY BROOK
STATE UNIVERSITY OF NEW YORK

ADVANCED ENERGY
RESEARCH AND TECHNOLOGY CENTER

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NATIONAL LABORATORY

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NATIONAL SCIENCE FOUNDATION

Industry/University Cooperative Research Centers

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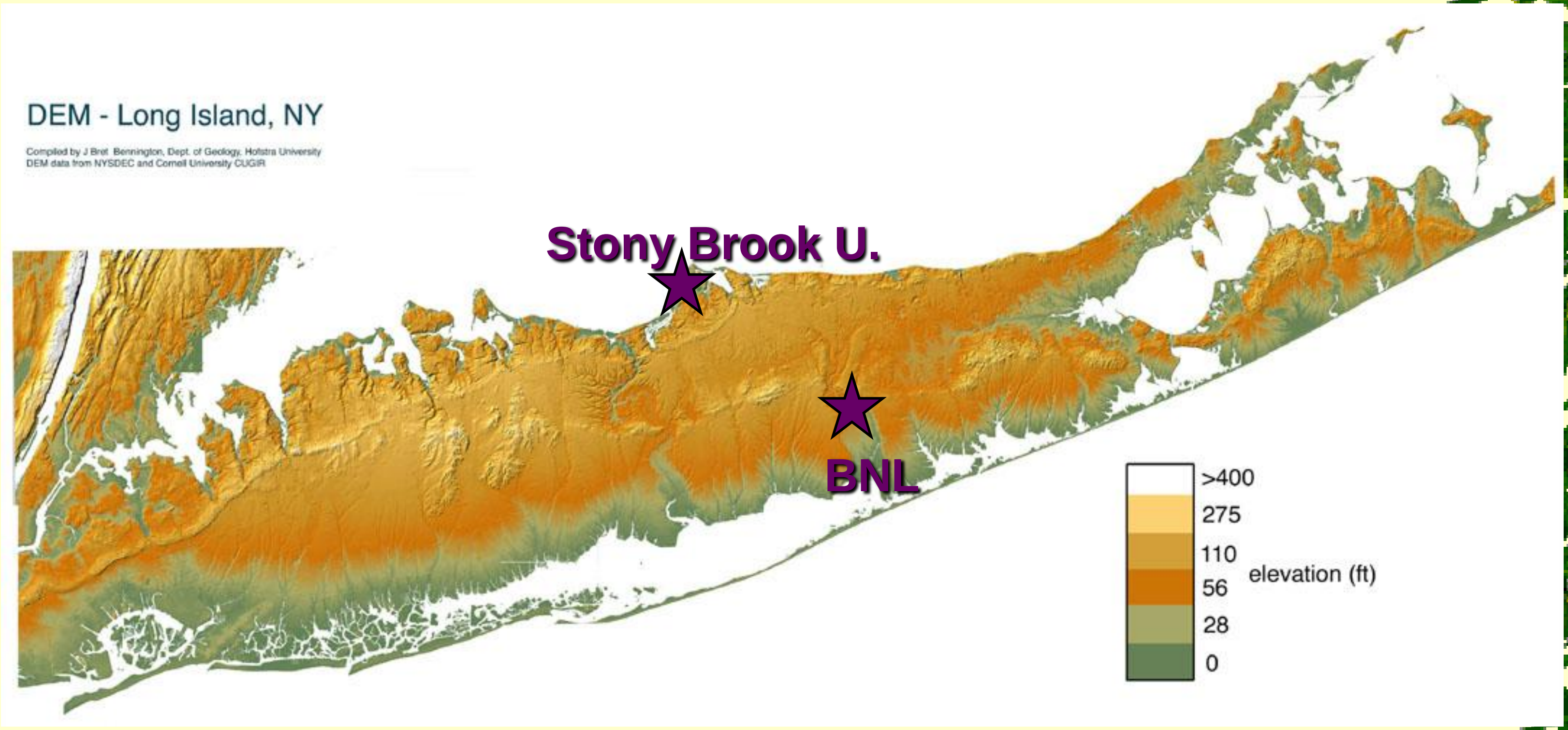
US DOE National Laboratories

Defense Program
Office of Science
Energy Efficiency and Renewable Energy
Office of Nuclear Energy
Fossil Energy

Our Location



The Future Fuels Group (BNL/SBU)

Students

Graduate

- M. Eaton (Exxonmobil)
- M. Anjom (SBU)
- P. Kerkar
- Y. Hung
- S. Patel

CME Undergrads

- 5-9 students/year

(SULI and Battelle Fellowships)

Collaborators

- CR Krishna (BNL)
- T. Butcher (BNL)
- N. van der Lelie (BNL)
- K. Ro (USDA)
- P. Hunt (USDA)
- C. Clayton (SBU)
- T. Koga (SBU)
- M. Rafailovich (SBU)
- H. Zhang (SBU)
- M. Castaldi (Columbia U.)
- R. Coffin (NRL)
- R. Kleinberg (Schlumberger)

Farmingdale State College

H. Tawfik

10+ Students

FUNDING

- National Science Foundation (NSF)
- U.S. Department of Energy (US DOE)
- BNL: Laboratory Directed R & D (LDRD)
- U.S. Department of Agriculture (USDA)
- SBU: Office of Vice President for Research
- Industry

SBU/BNL- Biomass Utilization Initiative

National Science Foundation- Engineering Directorate
I/UCRC (Industry/University Cooperative Research Center) Program

National Center for BioEnergy R&D (C-BERD)

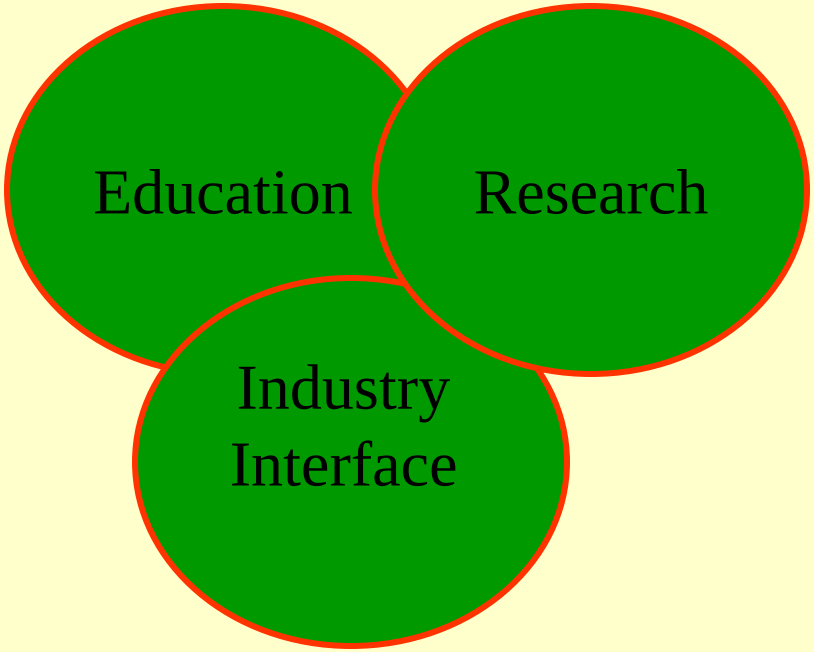
Founding Members

Kansas State University (K-State)
North Carolina State University (NCSU)
South Dakota School of Mines and Technology (SDSMT)
South Dakota State University (SDSU)
Stony Brook University (SBU)
University of Hawaii (UH)

Stony Brook Site- Industry Members

NYSERDA
National Grid
E-Renewables
Brookhaven National Laboratory
AERTC
Under discussion: 5

C-BERD Mission



Mission:
- To train students at all levels.
- Develop energy technologies based on renewables by working with industry.

National Center for BioEnergy R&D (C-BERD)

Features

National Biofuels Center
University consortium
Industry driven- Initially 50-70 industries are expected to join.
Industrial Advisory Board (IAB)

Focus Areas

Focus Area 1: Feedstock agronomy and supply
Focus Area 2: Feedstock breeding and genomics
Focus Area 3: Bioprocessing microbes and enzymes
Focus Area 4: Biomass processing
Focus Area 5: New platform technologies
Focus Area 6: Modeling and Process lifecycle analysis

Theme

Efficient Biofuels production and storage
Fuel utilization coupled with carbon sequestration

C-BERD: Sample Projects

- Biogas upgrading using membranes templated with supercritical (Sc) CO_2.
- Advanced concept in C sequestration: CO_2 recycling by catalytic conversion into bioalcohols.
- Ultra-deep (< 5 ppm) sulfur removal from biomass-derived fuels: The next-generation nano catalyst based technology.
- High conversion once-through catalysis: Biomass-derived syngas to renewable diesel.
- Advanced concept in C sequestration: CO_2 recycling by catalytic conversion into bioalcohols.
- Biofuel combustion: combustion characteristics and emissions.
- PEM fuel cells (Bipolar plate technology): efficiency management with bioalcohols as fuel feed.
- H_2 production by thermophillic bacteria.
- Interaction of biofuels with skin tissue: Potential toxicity of oxygenated fuels.

Biofuels

Definition: Fuels derived from CO_2-net neutral feedstocks.

Impact Sectors

- **Transportation**
- **Utilities**
- **Manufacturing**

Gasoline Consumption (2005): 140 billion gallons

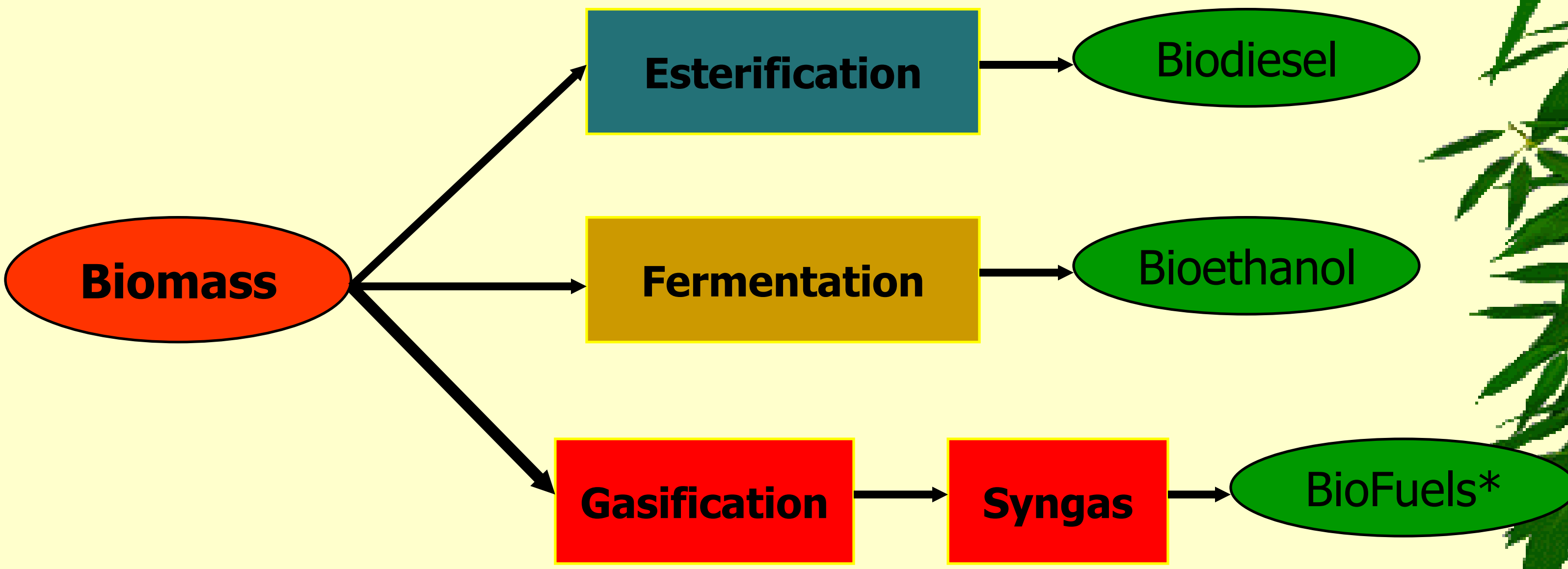
Biofuels Market Share (2005): 4% gasoline consumption

Target Fuel	2005/06	2007/08	2012	2025
	billion gallons/year		(Projected)	
Bioethanol [U.S.]*	5	8.8	7.5†	60
Biodiesel [U.S.]**	0.6	1.3		
Bioethanol [Brazil]**	4.5		4.5	

*Corn based; **Data from NBB; ***Sugarcane **based (45% of the world total);** †Projected in 2005

Goal: Replace 75% oil imports by 2025.

Biomass to Fuels



* Biofuels includes any liquid fuel

- Biorefinery concept is appealing because it will use the existing infrastructure.
- Biomass to BioFuels- Next-generation technologies are needed.

Biomass to Biodiesel

Biodiesel: Incentives for Expansion

- **Energy Act of 1992**
- **USDA Commodity Credit Corporation's (CCC) Bioenergy Program**

- **Energy Policy Act of 2005 [the Renewable Fuels Standard (RFS) phase-in]** – 2 Provisions
  1. <u>Supply Side</u>- Provide 10¢/gallon tax credit to small producers of biodiesel. Available for the first 15 million gallons produced by a plant with <60 million gallons annual production capacity.
  1. <u>Demand Side</u>- Fuel producers were required to include 4 billion gallons of renewable fuels by 2006, increasing to a minimum of 7.5 billion gallons by 2012.

- **EPA Diesel Regulations**

- Introduction of ultra-low sulfur diesel (ULSD)
- Biodiesel as lubricant additive (causes engine damage).
  - Addition of B2 restores lubricity.

Biodiesel: Production Methods

<u>Biodiesel Production Methods</u>

- **Base catalyzed transesterification of oil**
- Direct acid catalyzed transesterification of oil
- Convert oils into fatty acids and then to biodiesel

Biodiesel Production: The Reaction

Base catalyzed esterification reaction

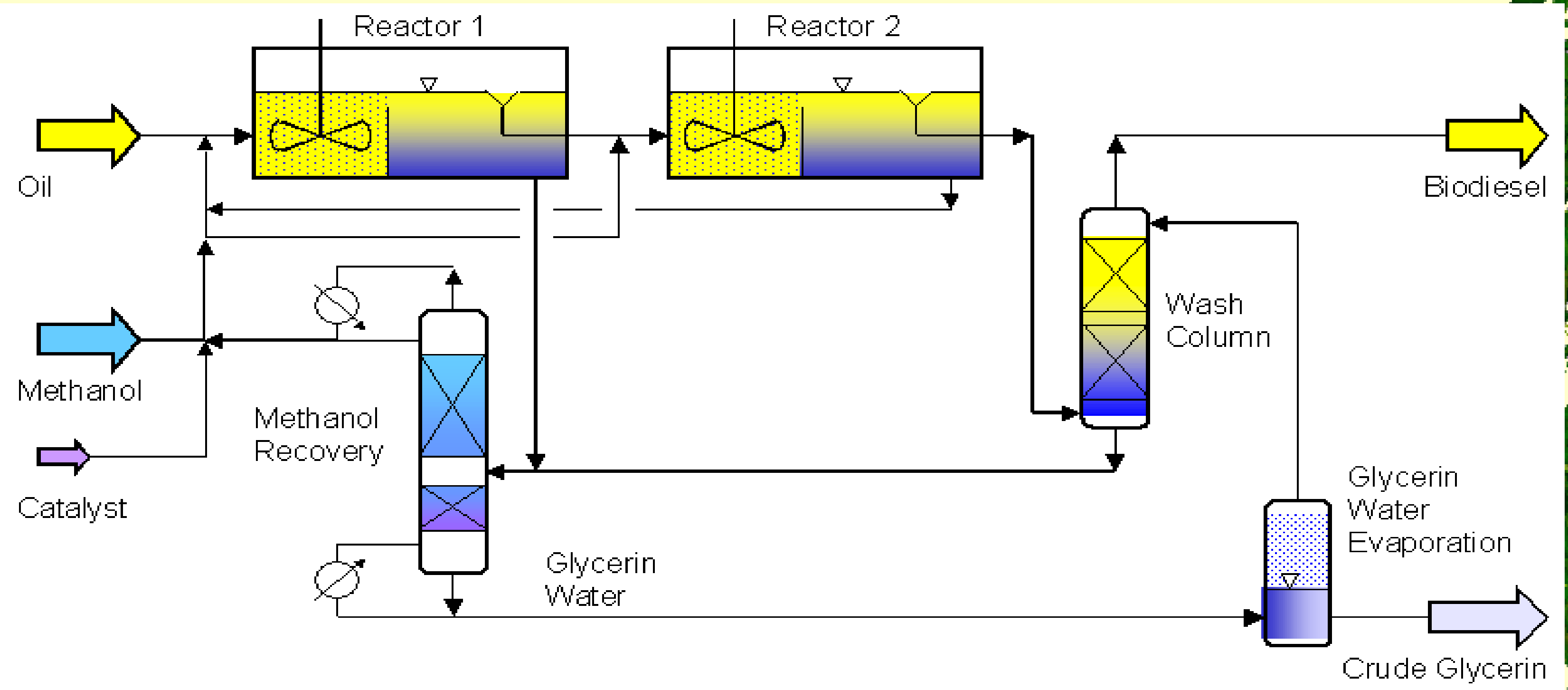
CH_2OCOR'''			CH_2OH		$R'''COOR$
$CHOCOR''$	+ 3 ROH	Catalyst →	$CHOH$	+	$R''COOR$
CH_2OCOR'			CH_2OH		$R'COOR$
(100 lbs)	(10 lbs)		(10 lbs)		(100 lbs)
Oil or Fat (Triglyceride)	Alcohol (excess)		Glycerin		Biodiesel Mono-alkyl **ester**

Oil or Fat: Soybean, Palmitic, oleic, stearic, linoleic acids
Catalyst: KOH, NaOH
ROH: MeOH, EtOH

- **Note the process needs MeOH or EtOH**

Biodiesel Production: The Flowsheet

Base Catalyzed Esterification of Oils



Source: Lurgi Process

Advantages

- Low T
- Low P
- Direct high conversion (~ 98%)

Biodiesel: Properties

ASTM Standard- D6751

- Reaction completion
- Glycerin removal
- Catalyst removal
- Free fatty acids removal

Fuel properties of biodiesel from Soybean oil

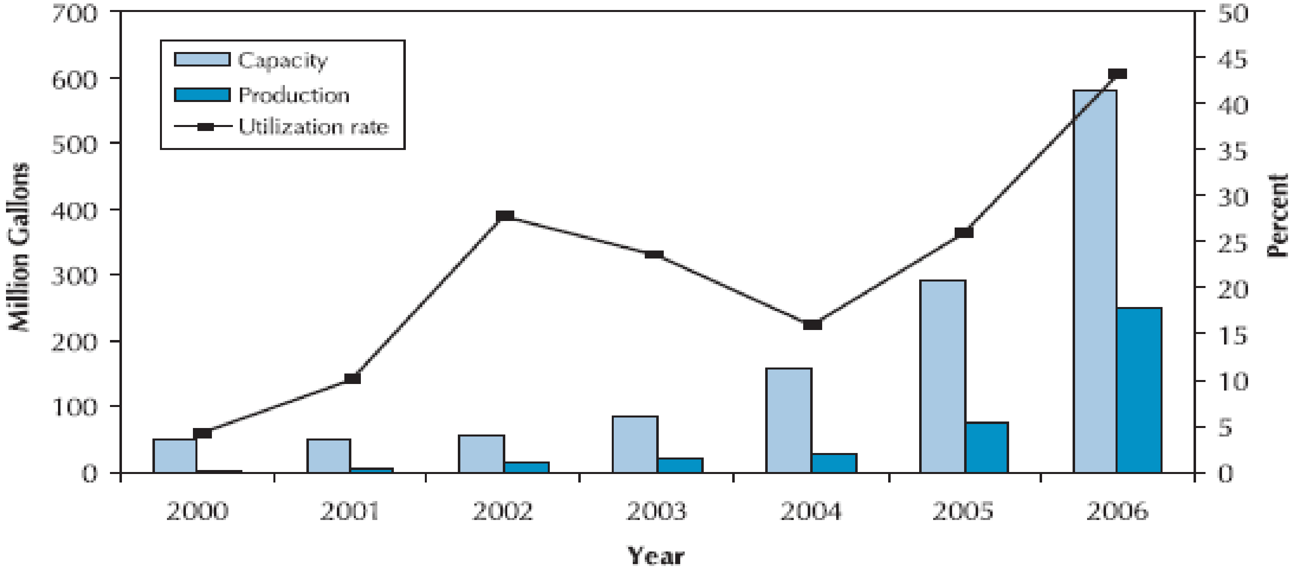
Ester	Viscosity mm^2/s	Cetane No.	ΔHg kJ/kg	T_{flash} °C	CP °C	PP °C
Methyl	4.08	46.2	39,800	191	2	-1
Ethyl	4.41	48.2	40,000	174	1	-4
Isopropyl		52.6	–	–	-9	-12
N-Butyl	5.24	51.7	40,700	185	-3	-7
No. 2 Diesel	2.39	45.8	45,200	78	-19	-23

ΔHg = gross heat of combustion; T_{flash} = flash point (Penske Martins closed cup); CP = cloud point; PP = pour point

Biodiesel: Fuel Quality for Diesel Engines

- ASTM Specification for B100 for Blending has been developed (D6751)
  - Changes being considered to improve quality
- Attempts are being made to address stability and compatibility with newer diesel technology concerns of engine manufacturers
  - Additional research required to define and test for stability
    - Lack of data relating stability and deposit formation in engine

Biodiesel: Production vs Capacity



Source: National Biodiesel Board.
Note: Capacity given is on September 1 of each year.

Figure 1. U.S. biodiesel production and installed capacity for 2000 to 2006

Source: Carriquiry, M. Iowa State U.

Biodiesel: Economics

<u>Assumptions</u>

- Plant size: 60 million gallons
- Feedstock cost: 80%
- 7.5 lbs feedstock/gallon biodiesel
- Operating cost (excluding feedstock): $0.42/gallon
- Credit for glycerin and other by-products: $0.05/gallon

Net operating profit = Revenues – Operating cost (excluding capital and other fixed costs)

Table 1. Net operating returns for a biodiesel plant

Biodiesel Price ($/gal)	Feedstock Price ($/lb) 0.20	0.25	0.30	0.35	0.40
2.00	0.16	-0.21	-0.59	-0.96	-1.33
2.40	0.56	0.19	-0.19	-0.56	-0.93
2.80	0.96	0.59	0.21	-0.16	-0.53
3.20	1.36	0.99	0.61	0.24	-0.13
3.60	1.76	1.39	1.01	0.64	0.27
4.00	2.16	1.79	1.41	1.04	0.67

Source: Carriquiry, M. Iowa State U.

► **<u>Problem</u>: U.S. biodiesel based on soybean oil**

Biodiesel Production- Challenges

- **Glycerol Utilization**
  - Better utilization of glycerin
- **Improve Esterification**
  - Processing steps
- **Fuel to diesel engine specifications**
  - Minimize impurities

Biomass to Bioethanol

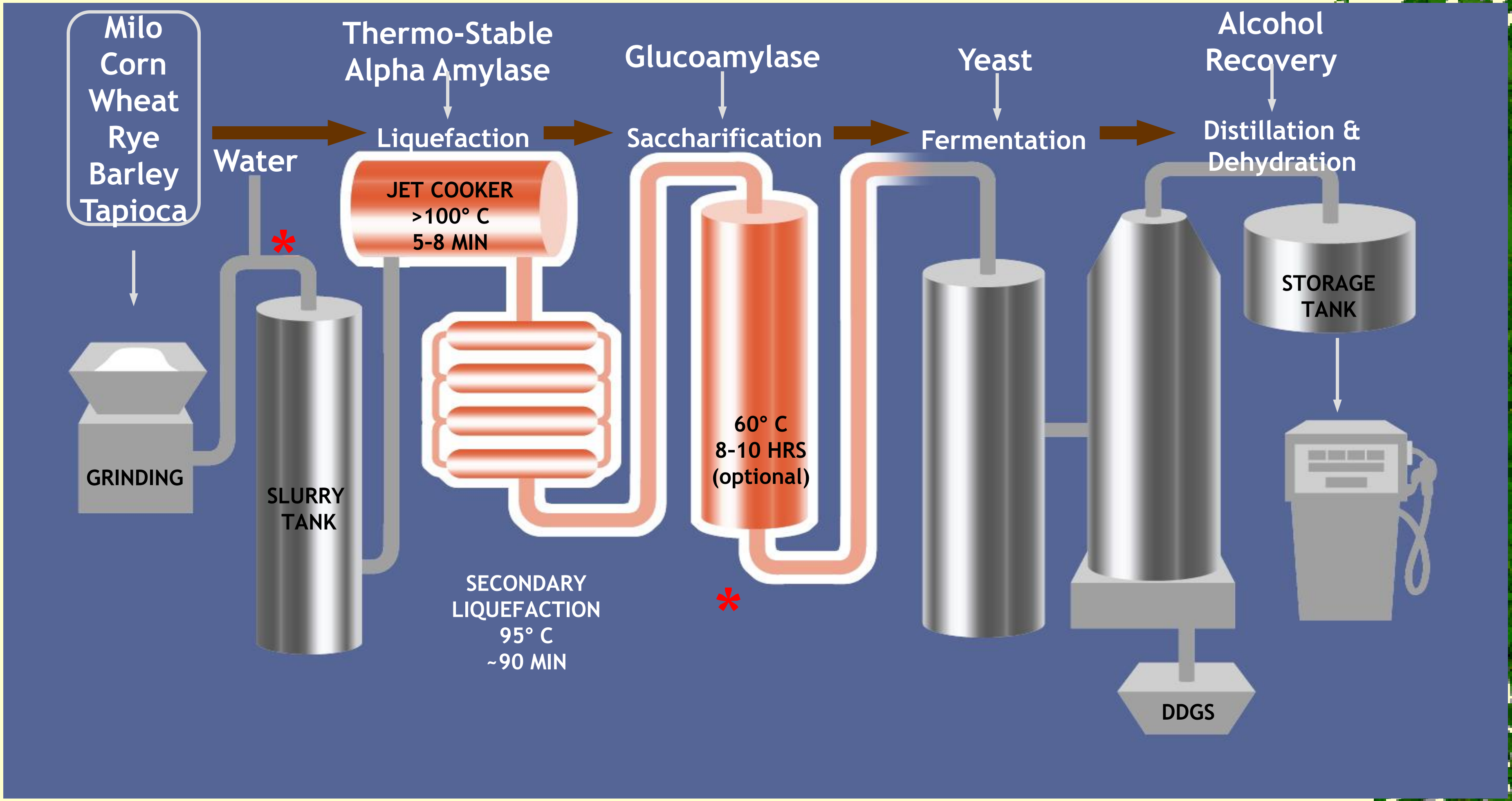
Bioethanol

$$C_6H_{12}O_6\ (aq) \xrightarrow{\text{Yeast}} 2\ C_2H_5OH\ (aq) + 2\ CO_2\ (g)$$

Glucose

- **Theoretical C Utilization: 67%**
- **CO_2: product of fermentation process**
- **Typical processing time: 48 hrs**

Bioethanol Production- Schematics



Source: Waste Conversion Technologies, UCLA

Bioethanol Production Data

Feedstock	Ethanol Recovery rate/Feedstock gallons/ton
Sugarcane	19.5
Sugarbeets	24.8
Molasses	
(Byproduct of Sugarcane/	
Sugarbeets	69.4
Raw sugar	135.4
Refined sugar	141
Corn Ethanol/bushel	
Wet milling	2.65
Dry milling	2.75
Ethanol yield	
Gallons/ton sucrose	
- Theoretical	163
- Expected	141

Data Source: USDA, 2006

Bioethanol Production: Economics

Data Source: USDA, 2006

Summary of estimated ethanol production costs, $/gallon)

Cost Item	Corn Milling Wet	Corn Milling Dry	Sugar cane	Sugar beets	Molasses	Raw sugar (3)	Refined sugar (3)	Brazil Sugar(4)	Brazil Sugar beets
Feedstock Cost(2)	0.40	0.53	1.48	1.58	0.91	3.12	3.61	0.30	0.97
Processing cost	0.63	0.52	0.92	0.77	0.36	0.36	0.36	0.51	1.92
Total Cost	1.03	1.05	2.40	2.35	1.27	3.48	3.97	0.81	2.89

1) Excludes capital costs.
2) Feedstock costs for U.S. corn wet and dry milling are net feedstock costs; feedstock costs for U.S. sugarcane and sugar beets are gross feedstock costs.
3) Excludes transportation costs.
4) Average of published estimates.

Present Bioethanol Production Data

Year	Capacity, Gallons
2000	1.6
2006	4.9
2009	11.5*

*Planned

Note: Ethanol energy content: 66% of gasoline

Source: FarmEcon.com (2007)

Present Bioethanol Production: Challenges

Process Related

• Inefficient utilization of feedstock (corn).

• Freshwater requirements for processing.

Humanitarian

• Food vs Fuel debate (recent riots in Asia and other countries with rising fuel prices).

• For each 1% rise in food prices, caloric intake among the poor drops 0.5% (World Bank Report).

• By 2025, 1.25 billion people will go hungry.

Summary- Ethanol and Biodiesel

Feedstock Issue

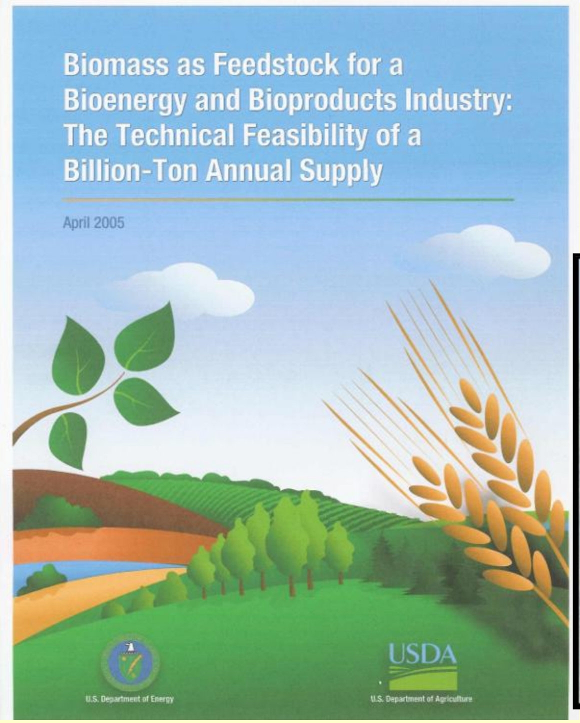
- Biodiesel: Vegetable oils and waste grease, etc
- Ethanol (U.S.): Corn based

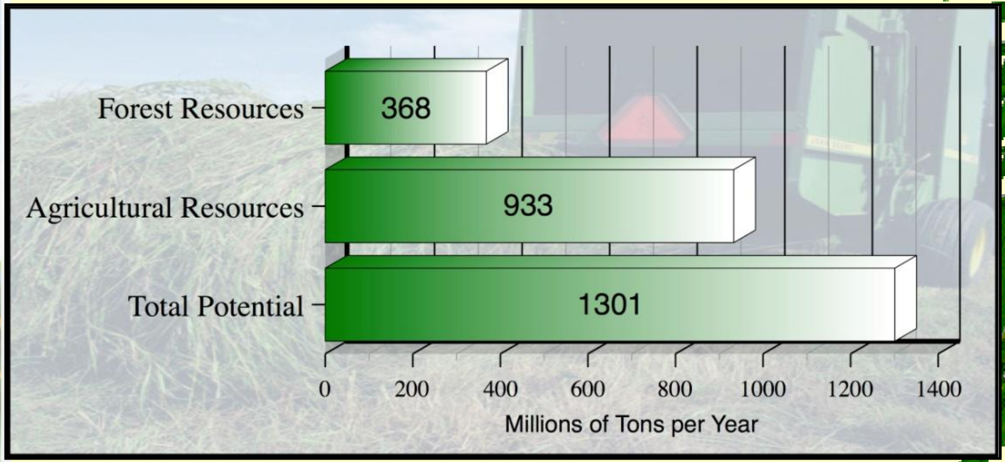
Biomass to Biofuels: Next Generation Technologies

Focus

- Maximize C conversion
- Non-food feedstocks

Biomass Feedstock



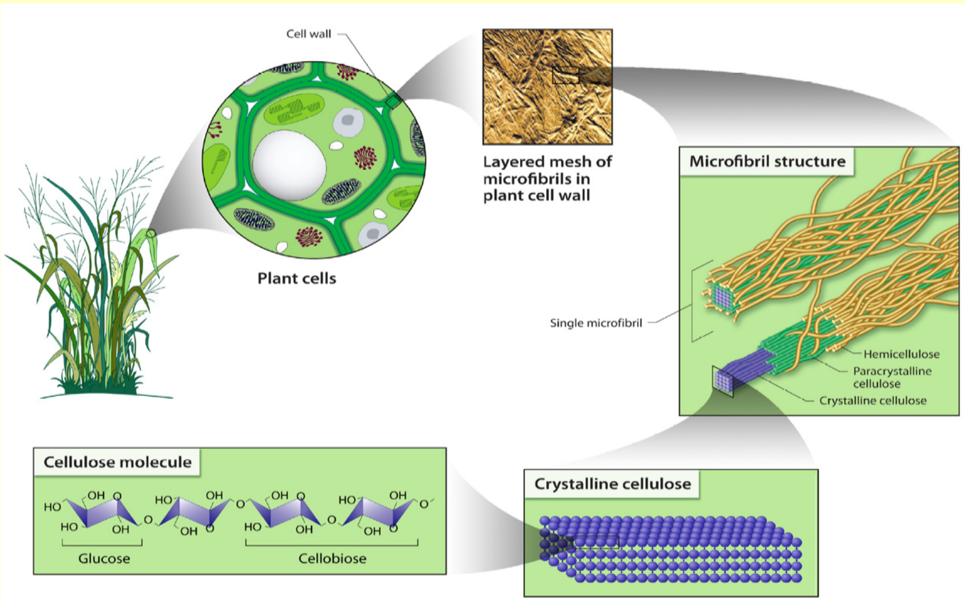


"Billion ton" study (USDA/DOE)

- **<u>Agriculture</u>**: Corn stover, wheat straw, soybean residue, <u>manure</u>, switchgrass, other energy crops.
- **<u>Forest</u>**: Forest thinnings, fuelwoods, logging residues, wood processing and paper mill residues, urban wood wastes.

Biomass: Structural Units

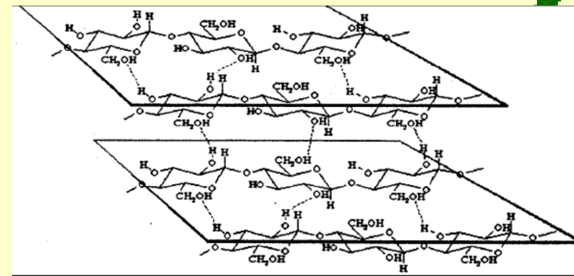
Source: US DOE



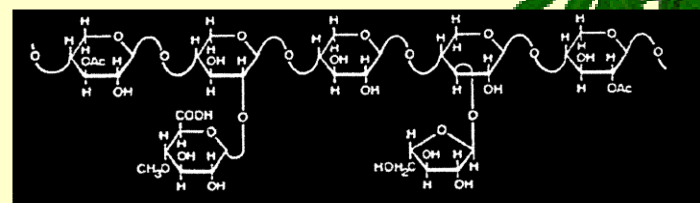
Typical composition

Carbohydrates/Sugars: 75%

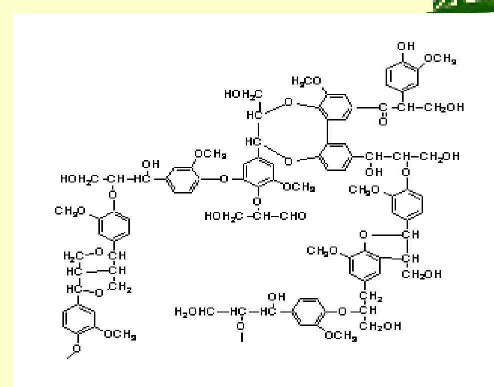
Lignin: 25%



Cellulose: Polymer and cross-linkages among glucose units.

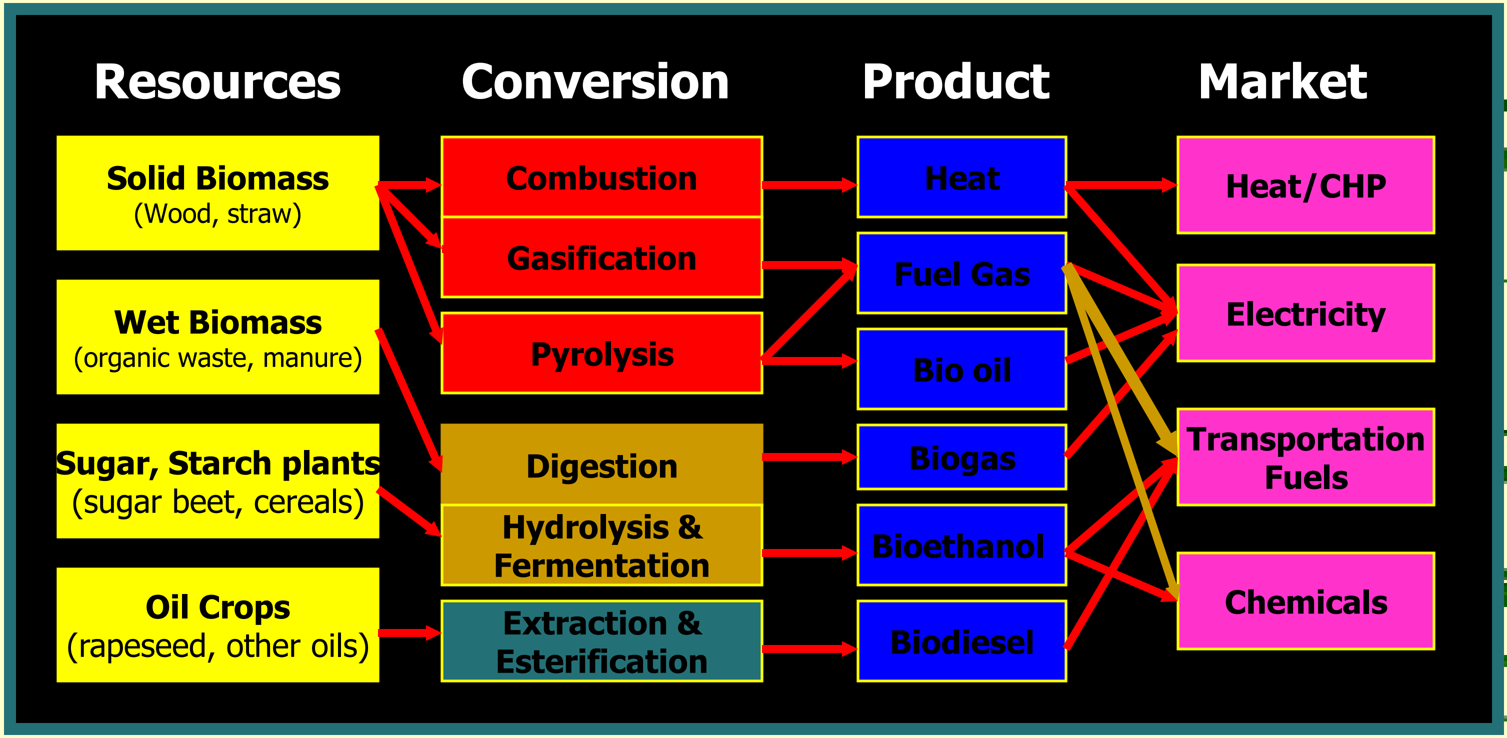


Hemicellulose: 5, 6 carbon sugars, sugar acids, acetyl esters- more complicated than cellulose.



Lignin: Phenolic polymers- impart strength to plants.

Biomass to Biofuels: Possible Routes



Source: Chemical Engineering, October 2006

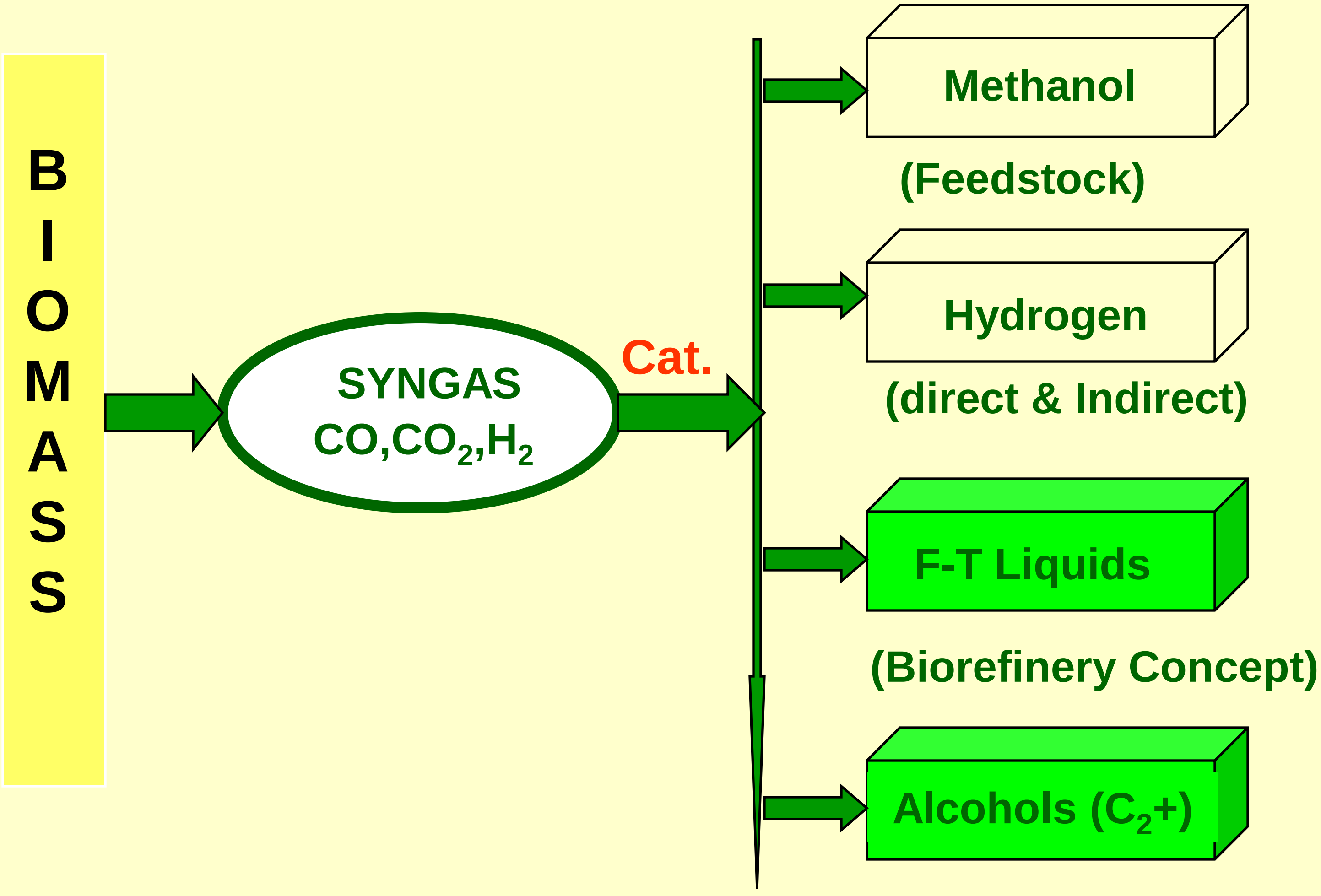
Driver: "Billion ton biomass is available in the U.S. (USDA/DOE Study).

Approach: Depolymerize biomass to 1C feedstock and then recombine ("Thermochemical" Pathway).

Product Focus: Transportation and Utility fuels

Biomass to Fuels

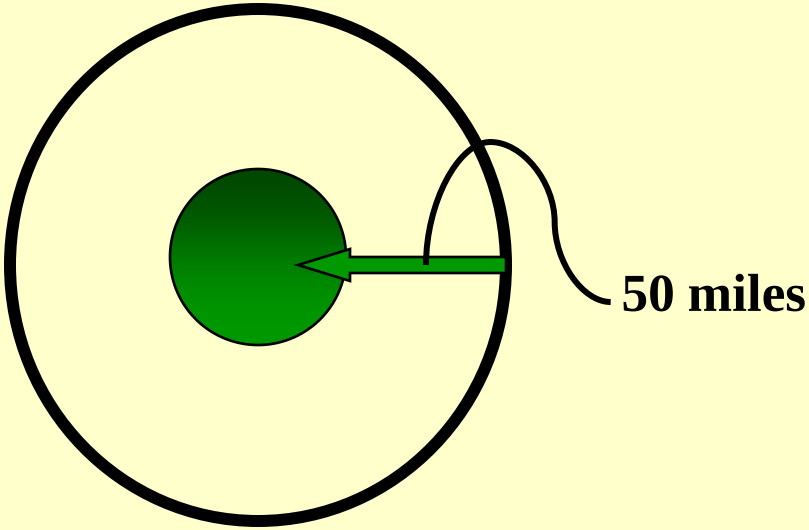
Thermochemical Route: Syngas Platform



Challenge: Total *Carbon* Utility with *Product* specificity.

Economical Biomass Processing- Targets

USDA Model



- **Biomass collection: 2000 T/d over 50-mile radius.**
- **Biofuel Yield (per dry ton):**
  - **Mixed Alcohols: 77 gallons/ton**
  - **F-T liquids: 3000 barrels /d**
- **Simple process:**
  - **No gas recycle**
  - **Managed gas clean up**
  - **Maximum per pass C conversion (DOE 2012 goal: 50%)**

Enabling Approach

<u>Goal</u>: Develop Atom-economical Processes

<u>Interdisciplinary</u>
Materials Science/Chemistry/chemical Engineering Interface
<u>Approach</u>
Combine Process Engineering and Process Chemistry

<u>Process Chemistry</u>
Liquid Phase Low Temperature (LPLT) concept
- Single-site or Nano catalysis

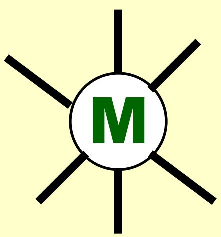
<u>Process Engineering</u>
Heat management
- Microchannel Reactors

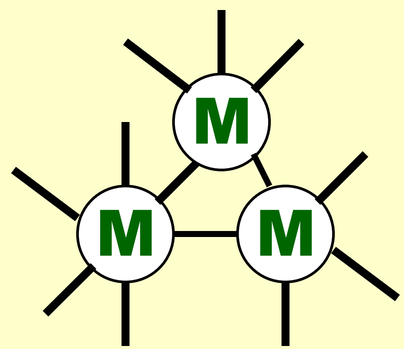
Liquid Phase Low Temperature (LPLT) concept

- Single-site or Nano catalysis

Controlled-site Catalyst**

Liquid Phase Operation ⟷ **Low Temperature**

Use Single site 

or Clusters 

Controlled-site Catalysts: Synthesis Methods

Characteristics of Nanoparticles of Interest

- **Produce in zero-oxidation state**
- **Convenient synthesis of nanoparticles.**
- **Potential to store nanoparticles for extended periods of time wi minimum degradation.**

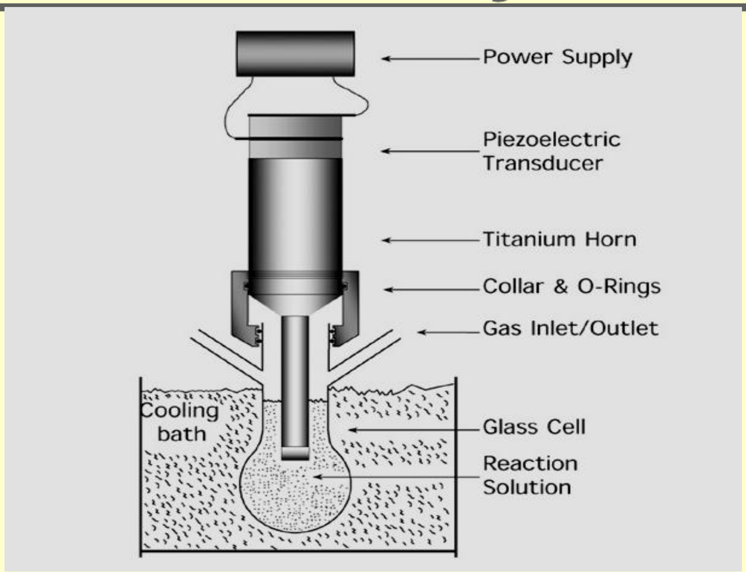
Potential Applications

- **Catalytic synthesis of Ultra-Clean fuels.**
- **Low-temperature nano coatings.**

☹ **Sonolysis and Thermal methods to synthesize nanoparticles.**

Sonolysis

Sonolysis Set-up



Theory (Suslick et al. Nature 353 414 (1991))

- **I**nvolves acoustic cavitation. During this event: T > 5000K and P > 120 MPa are reached within the cavity.
- Harness this energy to break chemical bonds:

$$M(CO)_n \rightarrow))) \rightarrow \text{nano “M”}$$

M: Mo, Fe

☹ **The naked metal (zero-Valent) can be further complexed to produce supported nanosized materials.**

XRD Data

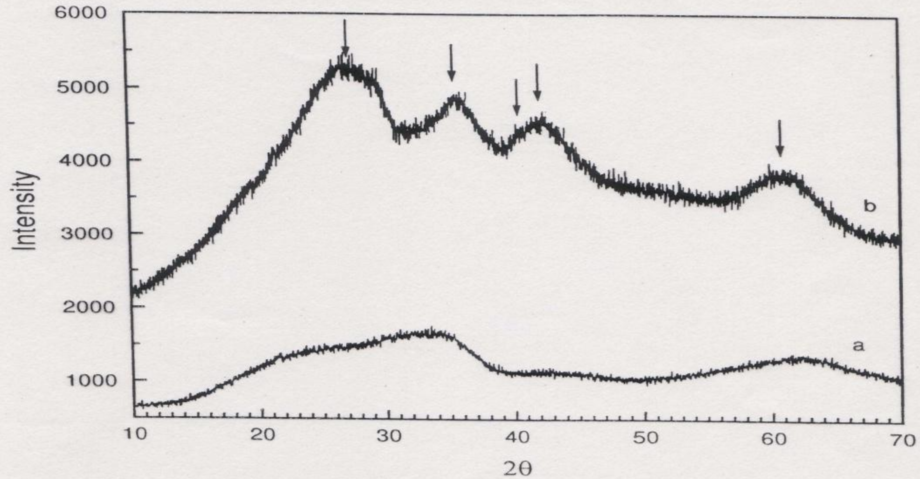
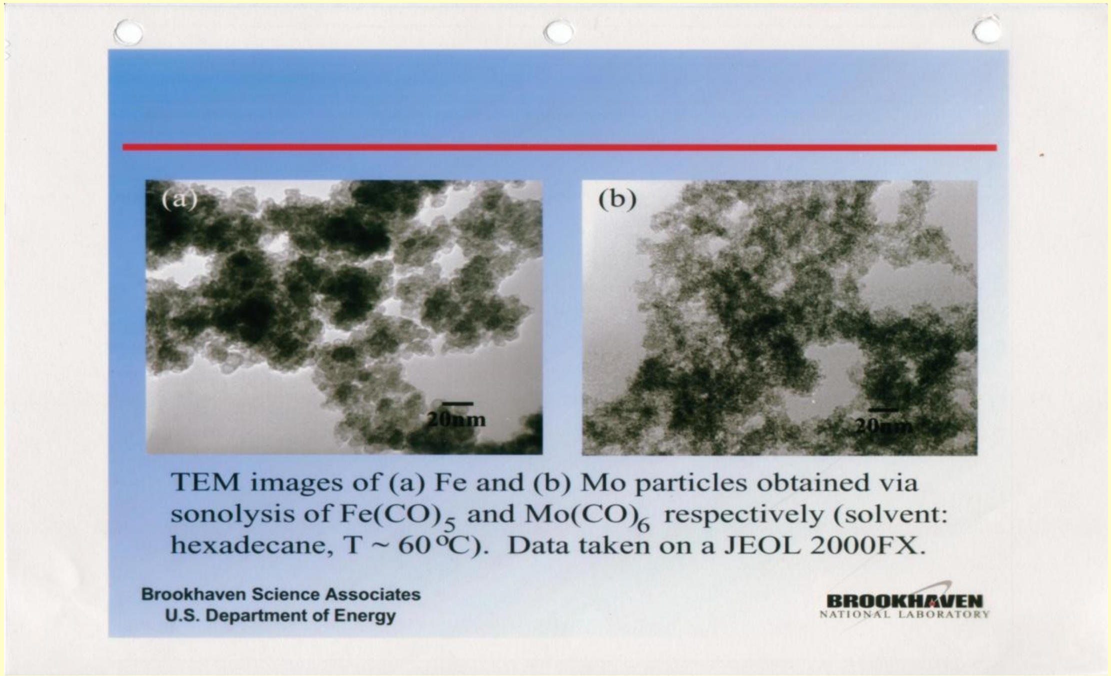


Figure 2. X-ray powder diffraction patterns of sonochemically produced samples of (a) Fe and (b) Mo (Sonolysis conditions: Solvent: Hexadecane = 100 mL; T = 53°C; $Fe(CO)_5$ = 8 mmol;;$Mo(CO)_6$ = 4 mmol).

- **Fe and Mo Nano-sized particles**

Sono Synthesis: TEM data of Fe and Mo



<u>Product specifications</u>

Fe: amorphous, MPD ~ 10 nm

Mo: Semi crystalline, MPD ~ 3 nm

Purity: > 99.9% (oxide impurity)

Fischer-Tropsch (F-T) Synthesis

F-T Reaction

$$CO + 2H_2 \rightarrow -(CH_2-)_n + H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Goal

Evaluate the activity of NANO-sized Fe-based catalyst for comparative performance.

F-T Data Summary

Catalyst loading = 4.6 wt%; Solvent: Ethylflopolyolefin-164; T = 513 K; P = 2770 kPa
H_2/CO = 66%/34%;GHSV = 4.6 NL g $Fe^{-1}.h^{-1}$; Run time = 120 h

Catalyst	NANO-2	NANO-1	MICRO
MPD, nm	3	20-80	32,500
CO conversion	42.9	55.9	65.4
H_2/CO usage	1.46	1.53	1.19
Product Distribution (wt %)			
HC	31.8	30.5	28.4
CO_2	31.7	39.0	46.6
H_2O	36.5	30.5	25.0
STY, $Kg.KgFe^{-1}.h^{-1}$	0.40	0.56	0.38

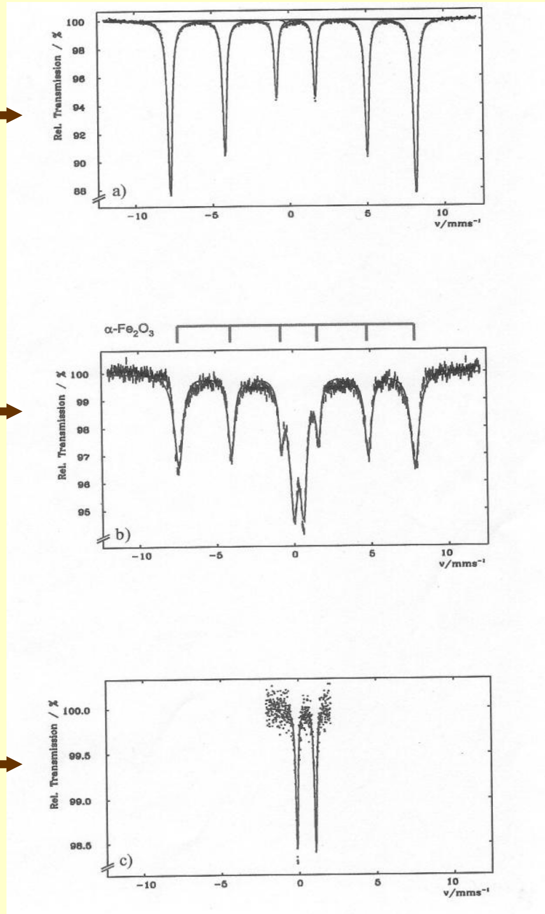
F-T Catalyst Characterization
^{57}Fe Mössbauer data

Fresh Samples at RT

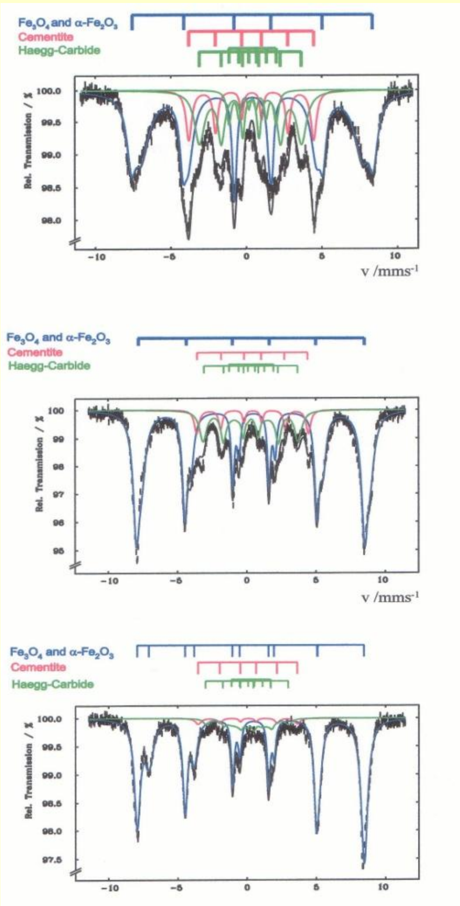
Nano-1 (20-80 nm)

Micro (32,500 nm)

Nano-2 (3 nm)



Quenched Samples



Micro (32,500 nm) 15K

Nano-1 (20-80 nm)

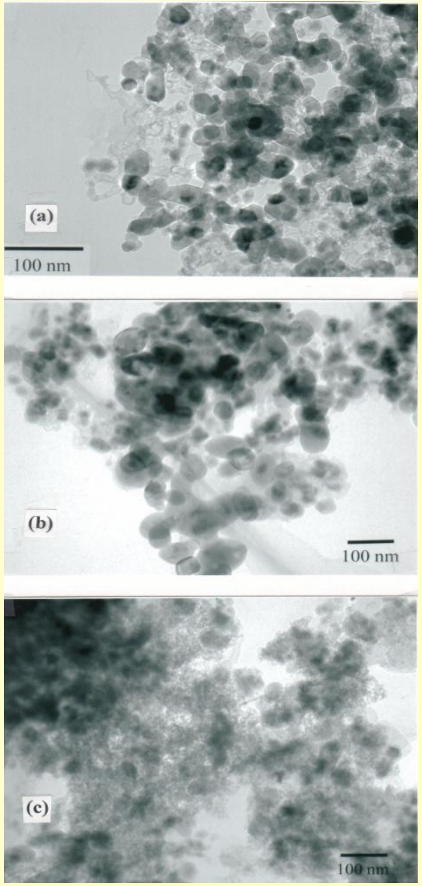
Nano-2 (3 nm)

TEM Data: Quenched Samples

Nano-2
(3 nm)

Nano-1
(20-80 nm)

Micro
(32,500 nm)



STY Versus Particle Size

T = 513 K, 120 h on-line

Material	Fresh nm	Quenched nm	STY $Kg.KgFe^{-1}.h^{-1}$
NANO-2	3	10-20	0.40
NANO-1	20-80	30-50	0.56
MICRO	32,5000	< 10	0.38

F-T Study: Observations

- TEM data show that micro materials transforms into the smallest size particles: Micro (< 10 nm) < Nano-2 (10-20 nm) > Nano-1 (30-50).
- Potential of using this technique for bulk production of nano metal particles.

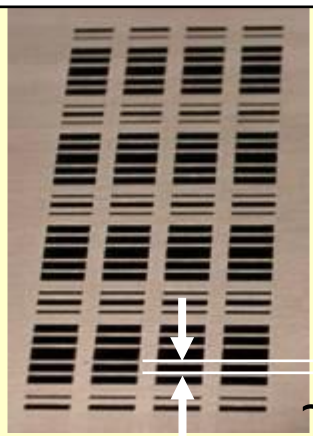
Process Engineering

Heat management

- Microchannel Reactors

Microchannel
vs
Conventional
Process Technology

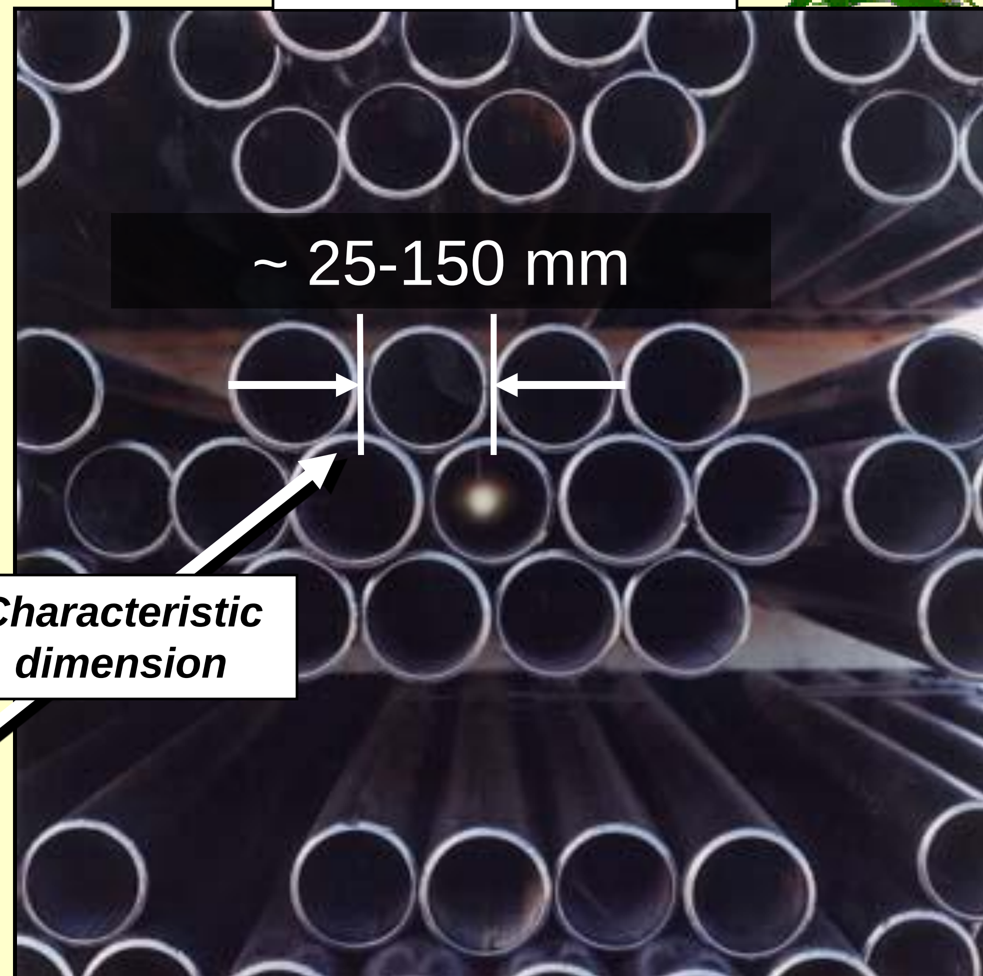
Microchannel



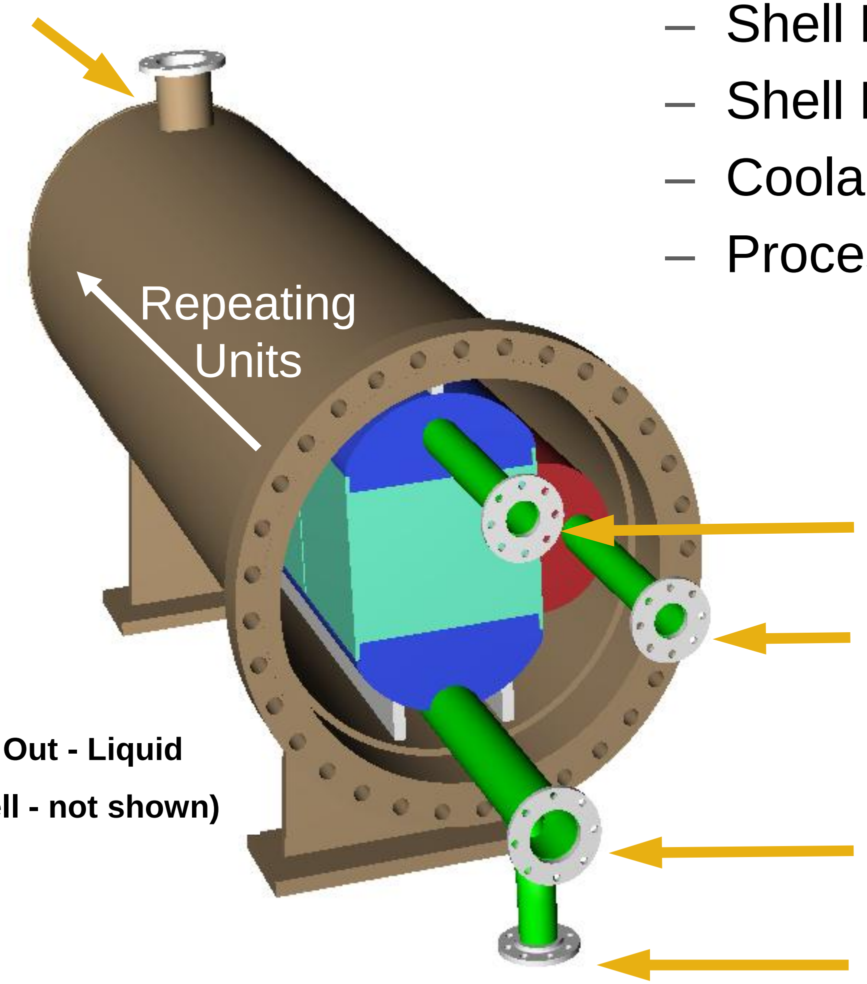
~ 0.1-
1.0 mm

Characteristic dimension

Conventional



Microchannel F-T Technology

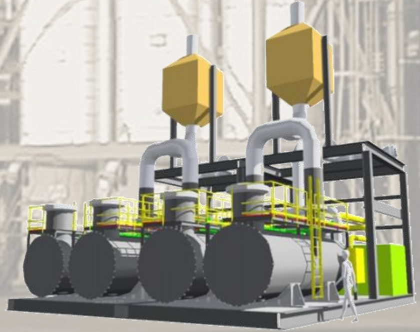


Specifications

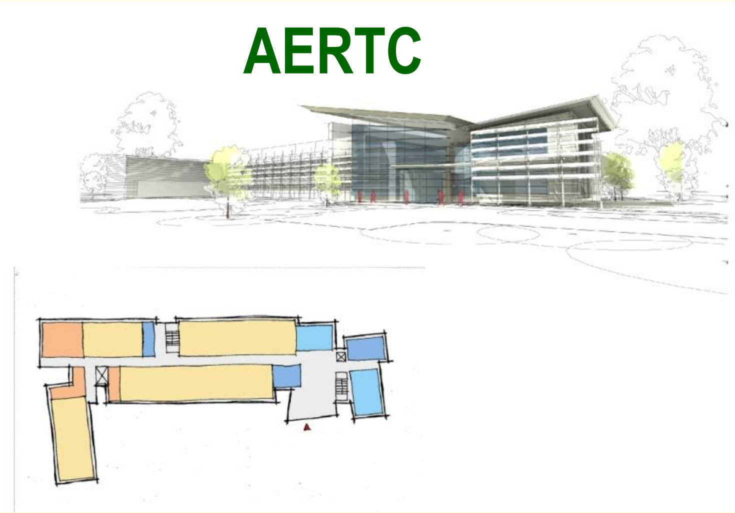
- Shell Diameter = ~1.25 m
- Shell Length = ~4 m
- Coolant flow length = ~0.6m
- Process flow length = ~0.6m

Velocys Steam Reformer

- Microchannel Reformer
- Same capacity
- 90% size reduction
- 33% capital cost reduction



Unique Facilities



<u>Research Facility</u>

- New York State funded $45 million at SBU.
  - Build the Advanced Energy Research & Technology Center (AERTC)
- NSF C-BERD will be housed in this building.

<u>Characterization Facilities</u>

- Center for Functional Nanomaterials **(CFN)**
  - A U.S. Department of Energy (US DOE) $85 million facility at BNL.

Biofuels: A Path to Sustainable Development

- Resource consideration
    - >1 billion ton biomass is available

- Distributive fuel production
    - “Small is beautiful”

- Process and related chemistry need to be integrated for Product flexibility
    - Closely related process chemistry

- “Oxygenates (Alcohols) Economy”- A transition to “Hydrogen Economy”

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- U.S. Department of Energy.
- AERTC Seed Grant.
- **Industry**

A Path forward for Liquid Biofuels

Motivation

- Past
  - Remote natural gas conversion pathways.
  - Coal-based IGCC power plants: peak-shaving fuel

- Present
  - Biomass conversion

-Finding sustainable sources of ENERGY is a global problem.

C-BERD

Industry

University

Events

2008 Advanced Energy Conference
Long Island

2008
November 19-20

2009
November 18-19

www.aertc.org