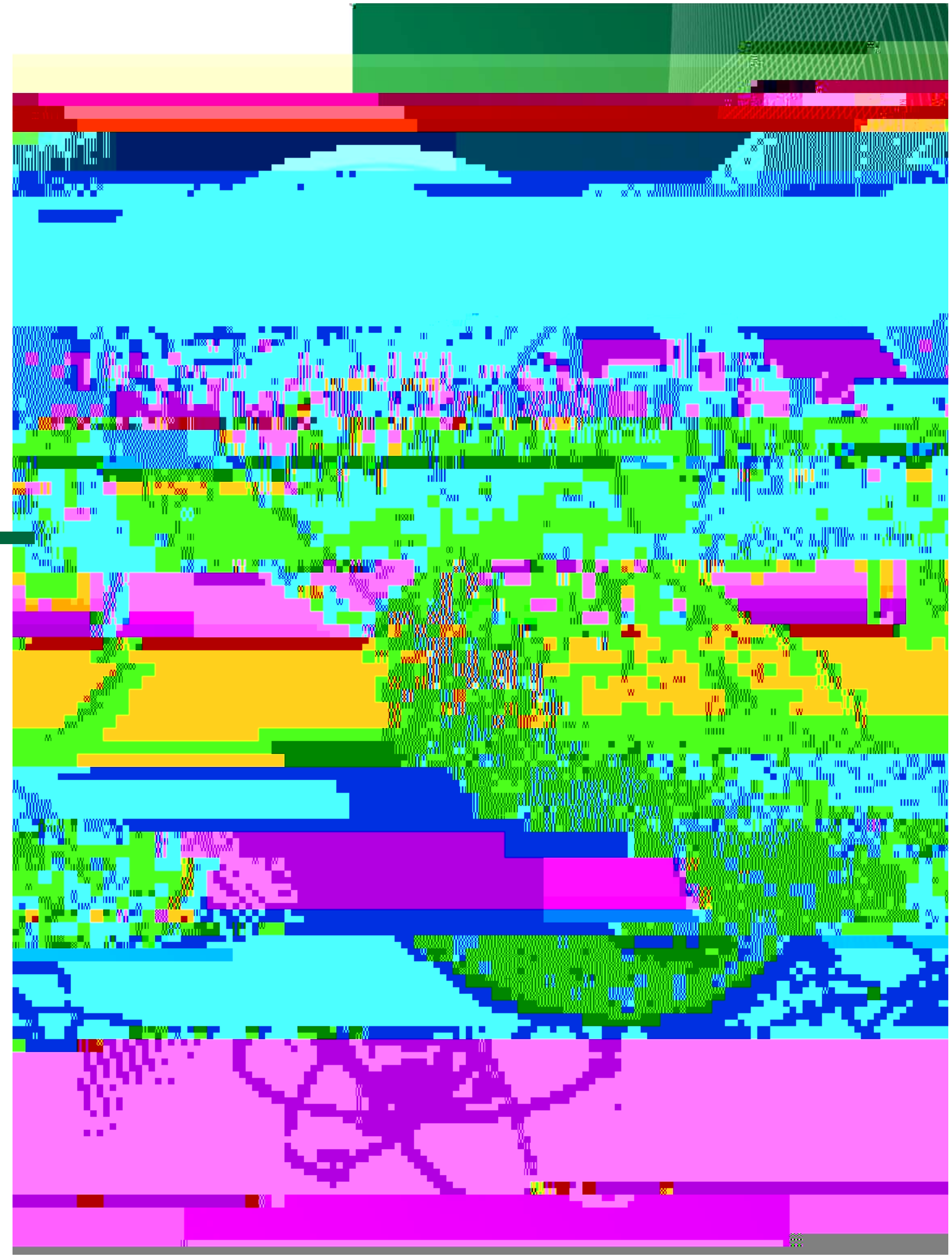
Cellulosic Biofuels: continued R&D challenges during pioneer biorefinery deployment



Brian H. Davison,

Oak Ridge National Laboratory

BioEnergy Science Center

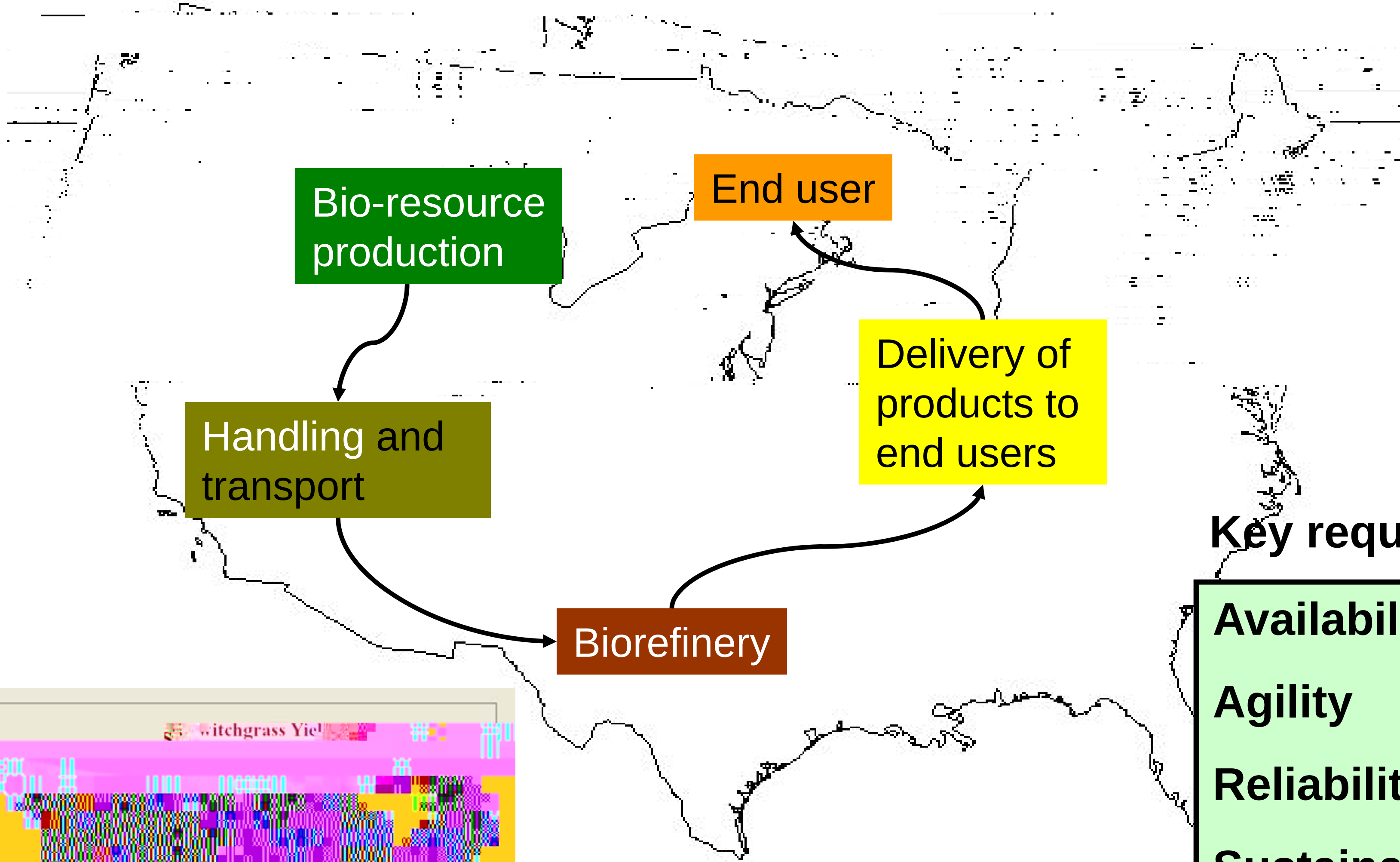
Presented to AIChE Knoxville

November 19, 2015

Why still biofuels?

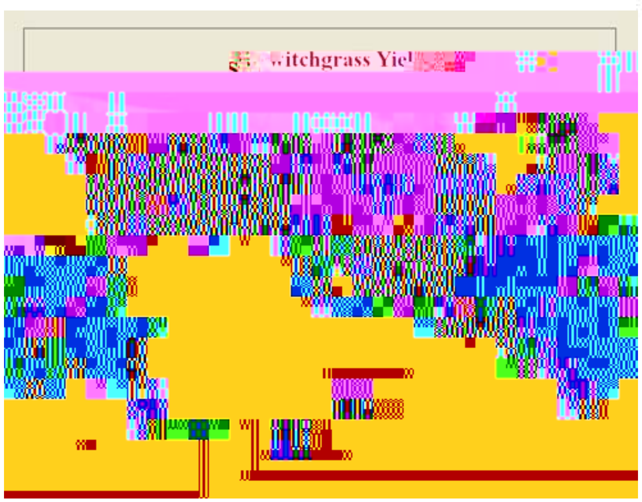
- The unique role for biomass
  - *"… Biomass is our only renewable source of carbon-based fuels and chemicals"* – Ray Miller, DuPont, 2005
  - Essential for liquid based transportation fuels (gasoline, diesel, and especially jet)
- An important part of most broad assessments and scenarios for a low-carbon future
- The potential capacity exist for significant impact in magnitude and sustainabililty

Bioenergy is analogous to other existing energy networks



Key requirements

- **Availability**
- **Agility**
- **Reliability**
- **Sustainability**
- **Security**



Biomass Utilization is a multi

Biomass Utilization: current Corn Bioethanol

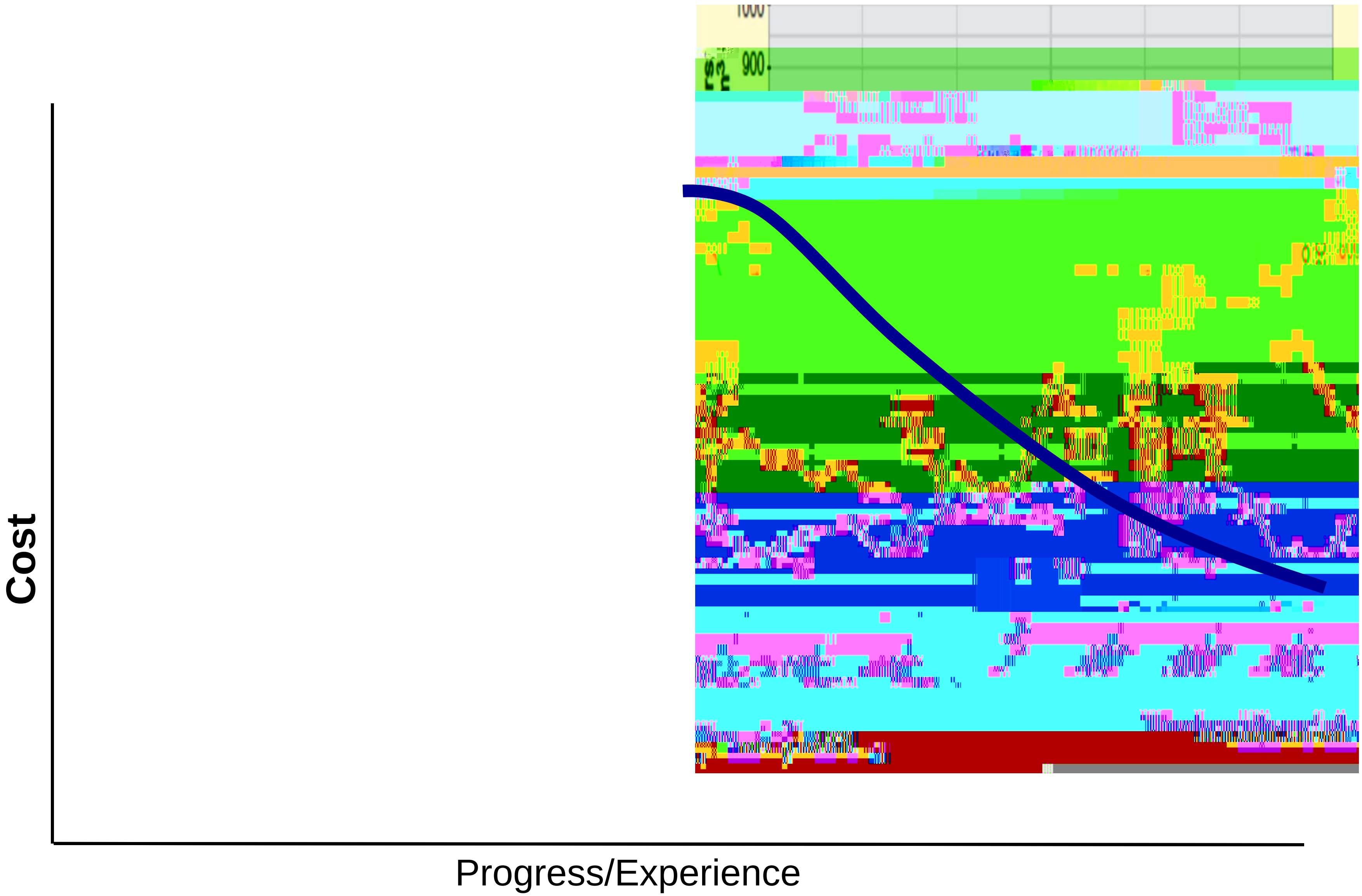
LAND	Feedstocks	Process technologies	Output/Products
Current cropland	Grain crops (Corn)		Ethanol
Fallow land (CRP, etc)	softwood	pulping	diesel
Marginal land	switchgrass	gasification	
Rangeland	Animal wastes	Thermo/chemical conversion	
Forestland	Agric. residues	Anaerobic digestion	
	bagasse	Other	
	Oil crops		

Biomass Utilization: Gov. Bredesen's

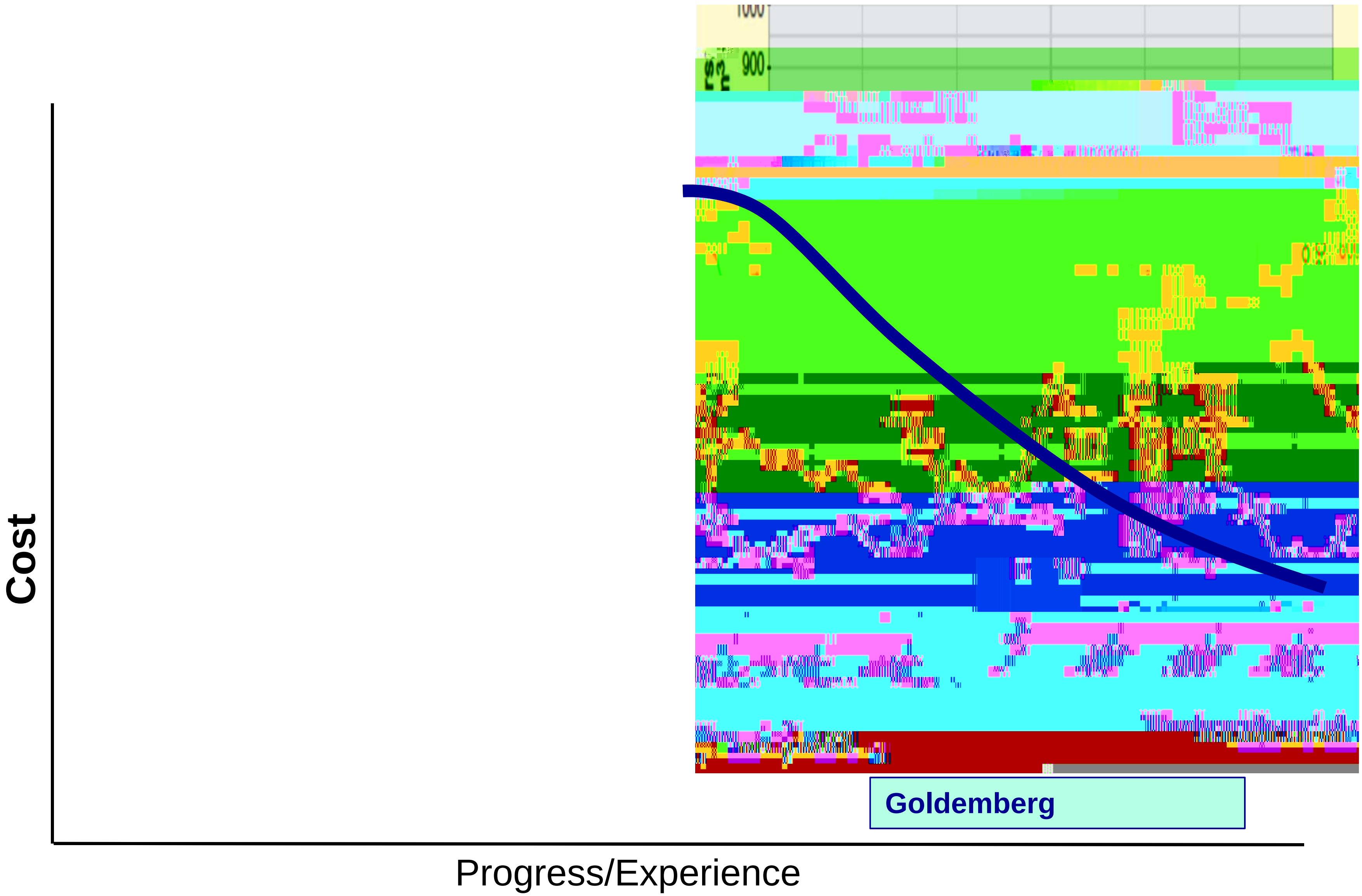
Critical factors affecting deployment and scale-up of U.S. bioenergy industries

Feedstocks	Logistics and Land-Water Use	Conversion Technologies	Products and Utilization
Insufficient yield	Spatially dispersed feedstock sources	Insufficient yield, rate, and titer	Biofuel demand - ethanol blend wall, development of new biofuels (e.g., bioJet)
Tolerance to environmental stresses (e.g., drought)	Low bulk density and high moisture content of feedstock	Feedstock composition (e.g., recalcitrance)	Compatibility with existing infrastructure
	ecos T10Twbulk dens Tw3iskg., drosourcld	infrap75 3ld	

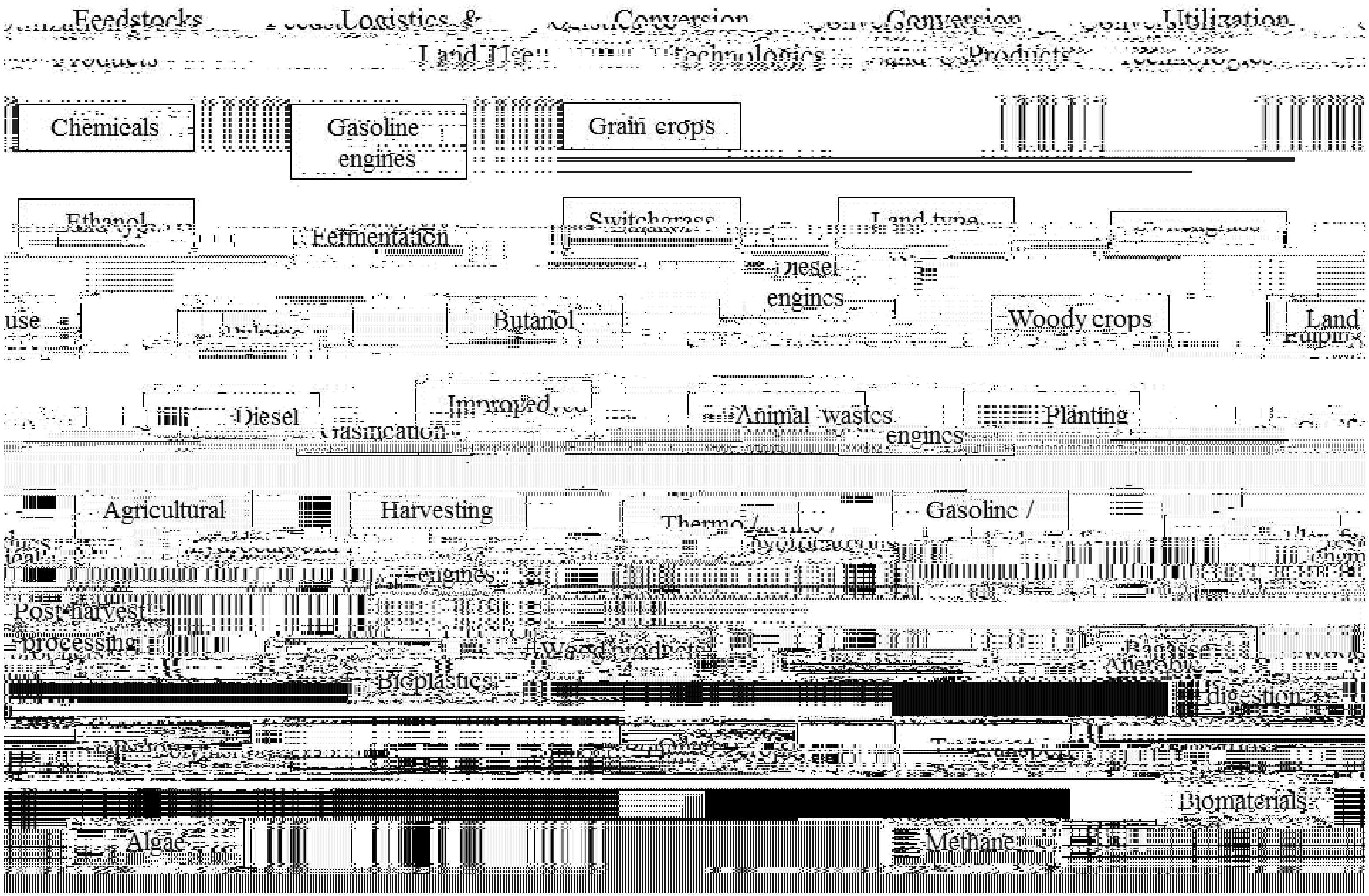
c7Qqu289.2c-289.2c0 9c-89.2c0 9c.4.272s 0 0 0



Brazil 1st Gen Ethanol Curve



Major components of the biofuels supply chain



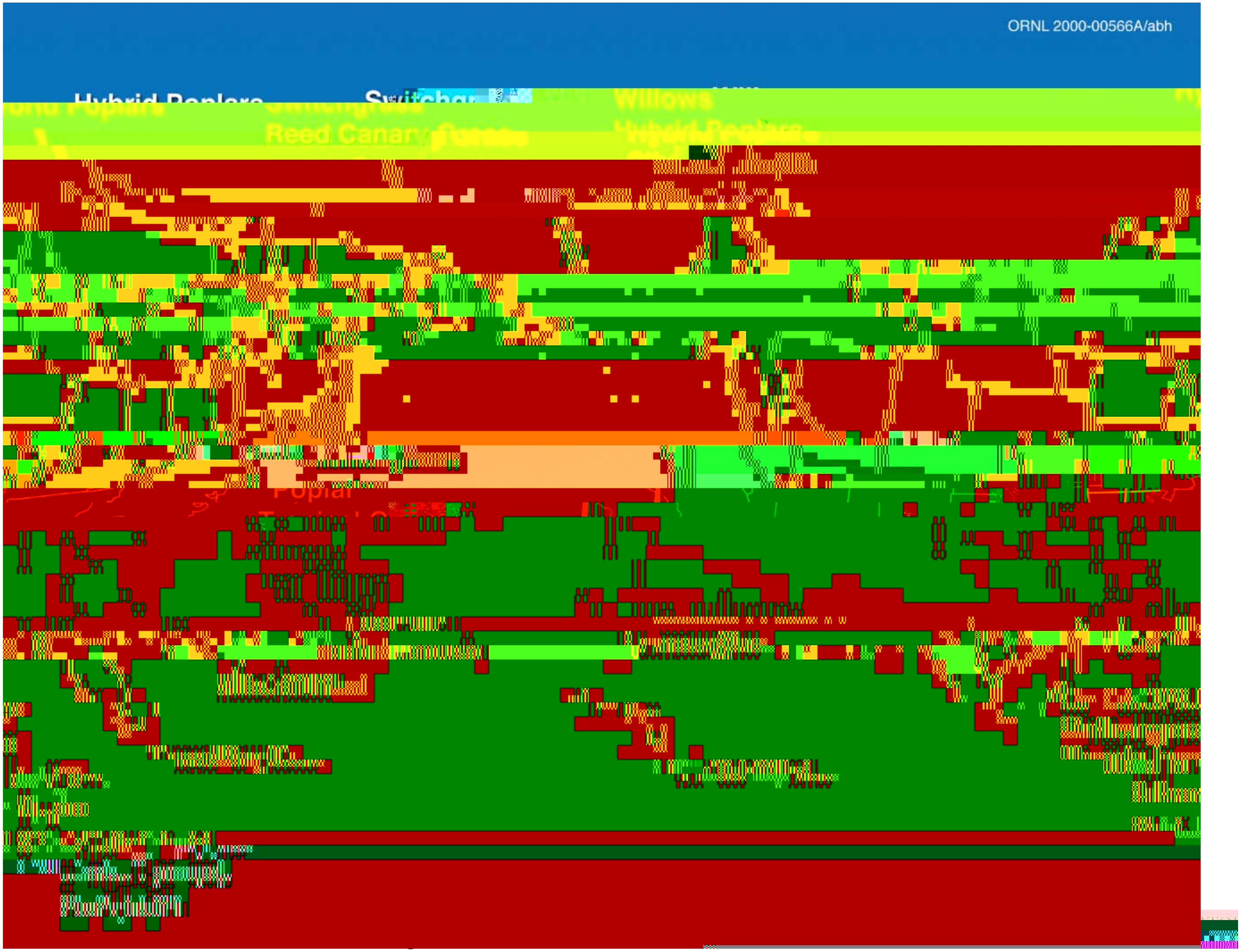
Bioscience and biotechnology for sustainable mobility

Are there sufficient amounts of biomass?

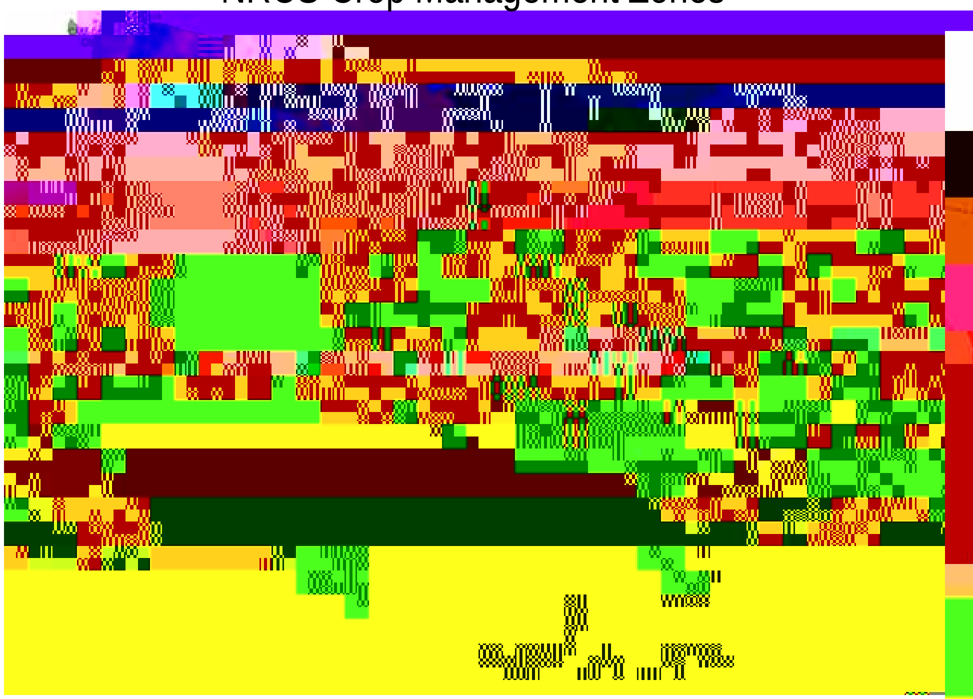
- Yes, land resources of the U.S. can sustainably supply more

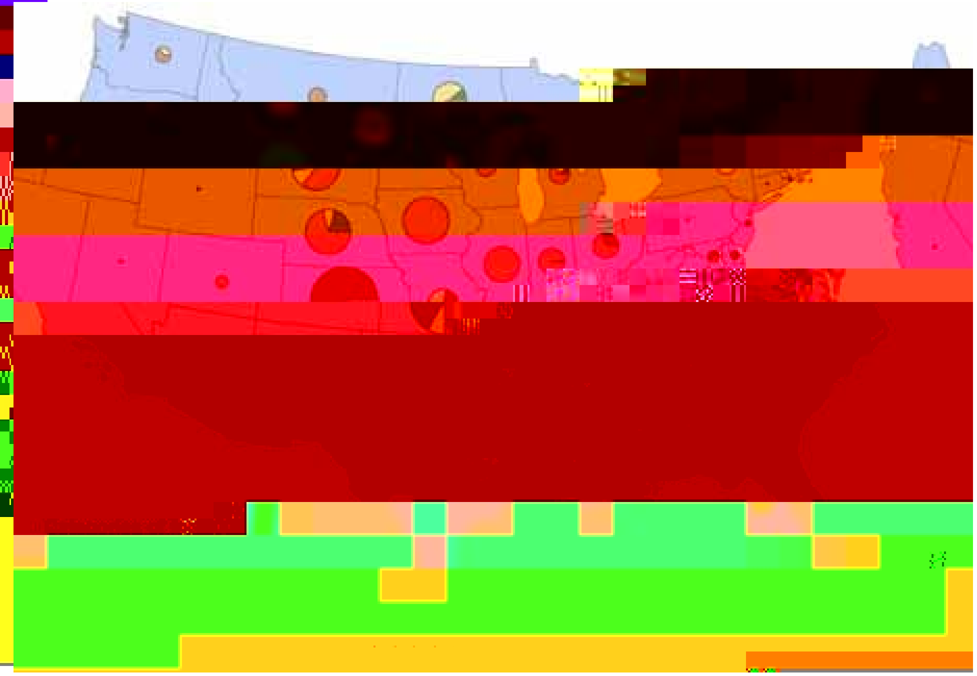
Robert Perlack, Lynn Wright, Anthony Turhollow, Robin Graham (ORNL); Bryce Stokes, Donald Erbach (USDA)

Geographic distribution of biomass crops

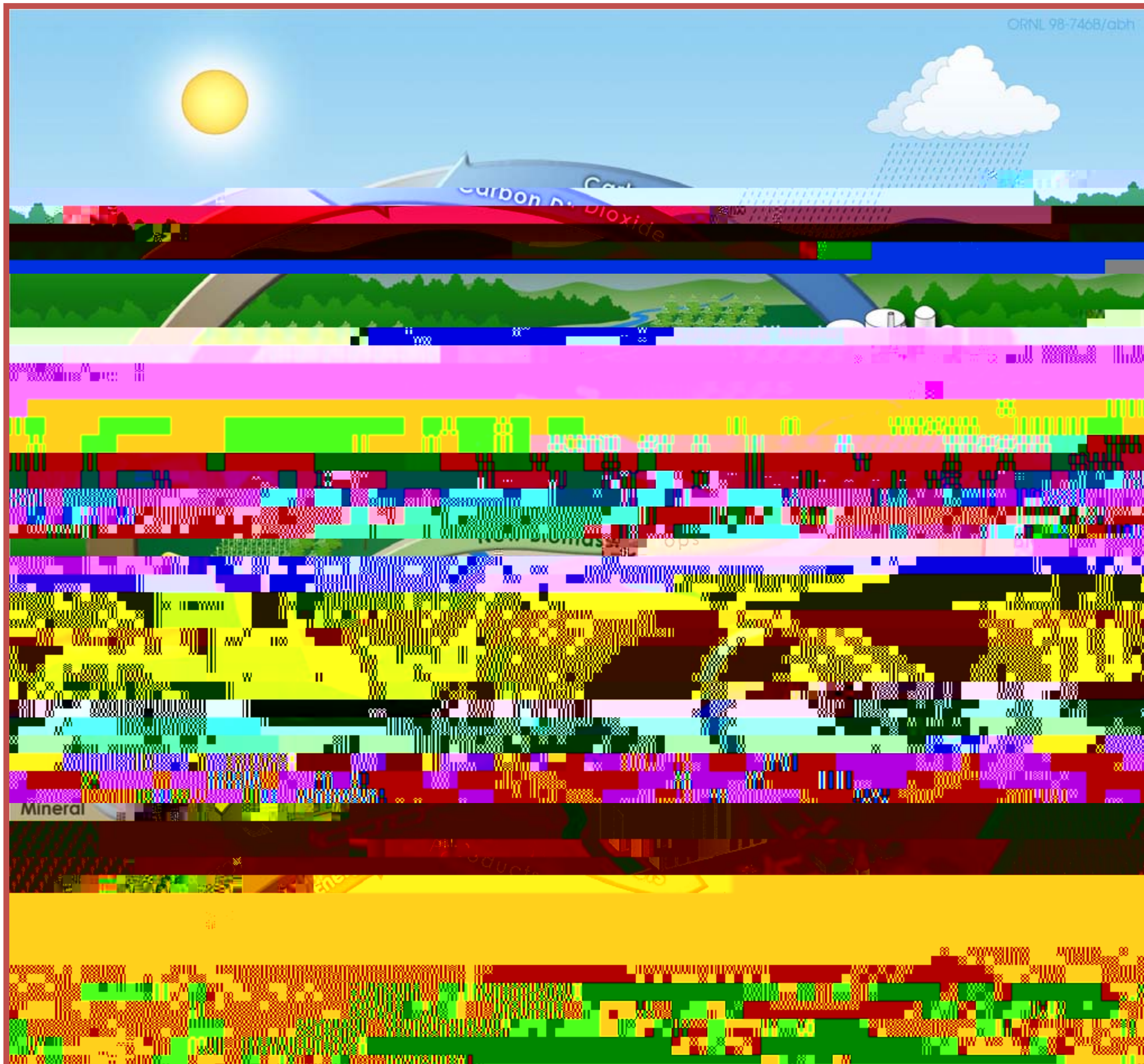


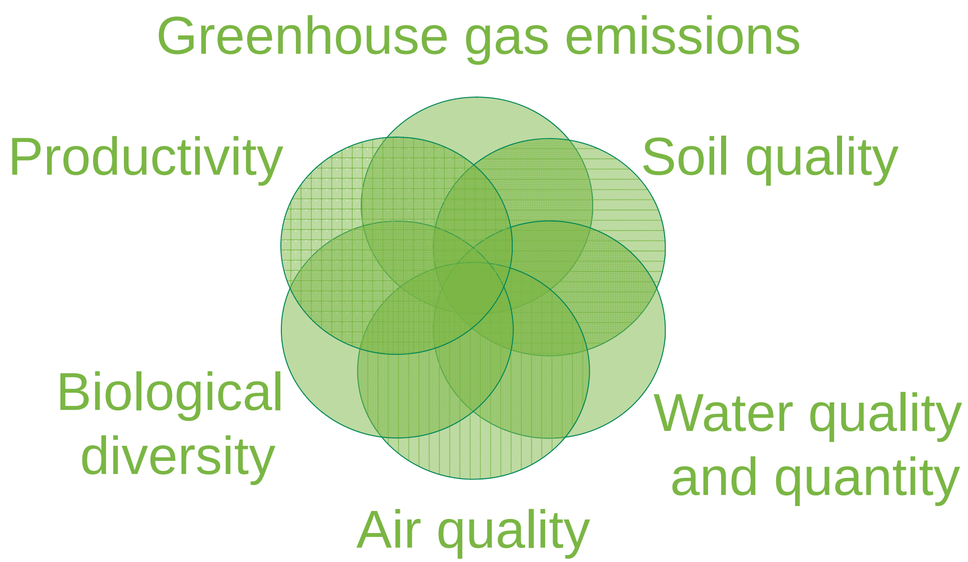
NRCS Crop Management Zones

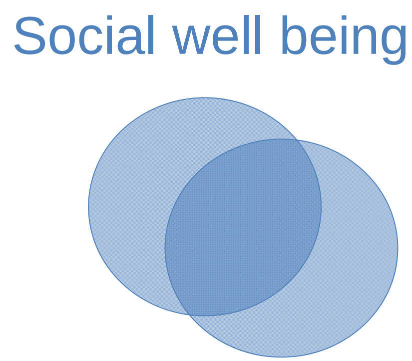




Can this system be sustainable?




Greenhouse gas emissions
Productivity
Soil quality
Biological diversity
Water quality and quantity
Air quality

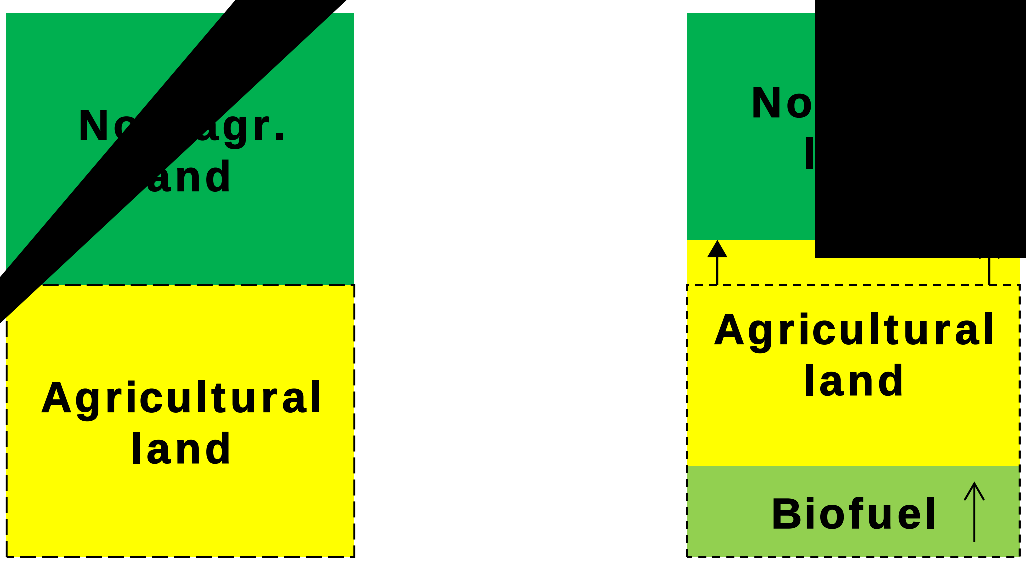

Social well being

Identified Indicators of Environmental Sustainability

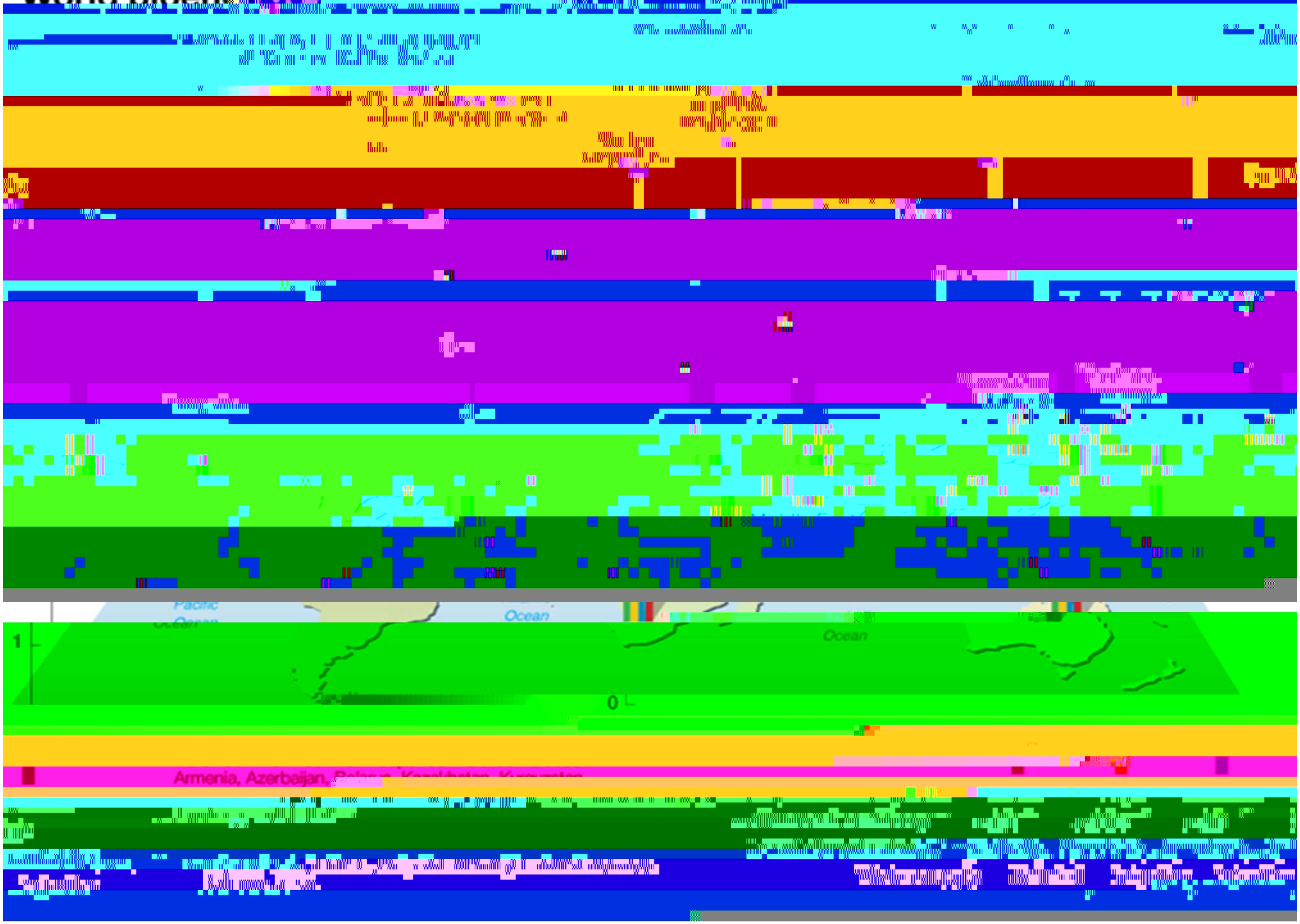
Category	Indicator	Units
Soil quality	1. Total organic carbon (TOC)	Mg/ha
	2. Total nitrogen (N)	Mg/ha
	3. Extractable phosphorus (P)	Mg/ha
	4. Bulk density	g/cm^3
Water quality and quantity	5. Nitrate concentration in streams (and export)	concentration: mg/L; export: kg/ha/yr
	6. Total phosphorus (P) concentration in streams (and export)	concentration: mg/L; export: kg/ha/yr
	7. Suspended sediment concentration in streams (and export)	concentration: mg/L; export: kg/ha/yr
	8. Herbicide concentration in streams (and export)	concentration: mg/L; export: kg/ha/yr
	9. storm flow	L/s
	10. Minimum base flow	L/s
	11. Consumptive water use (incorporates base flow)	feedstock production: m^3/ha/day; biorefinery: m^3/day

Category	Indicator	Units
Greenhouse gases	12. CO_2 equivalent emissions (CO_2 and N_2O)	kgC_{eq}/GJ
Biodiversity	13. Presence of taxa of special concern	Presence
	14. Habitat area of taxa of special concern	ha
Air quality	15. Tropospheric ozone	ppb
	16. Carbon monoxide	ppm
	17. Total particulate matter less than 2.5 m diameter ($PM_{2.5}$)	$\mu g/m^3$
	18. Total particulate matter less than 10 m diameter (PM_{10})	$\mu g/m^3$
Productivity	19. Aboveground net primary productivity (ANPP) / Yield	gC/m^2/year

McBride et al. Indicators to support environmental sustainability of bioenergy systems. *Ecological Indicators 11:*1277-1289 (2011)

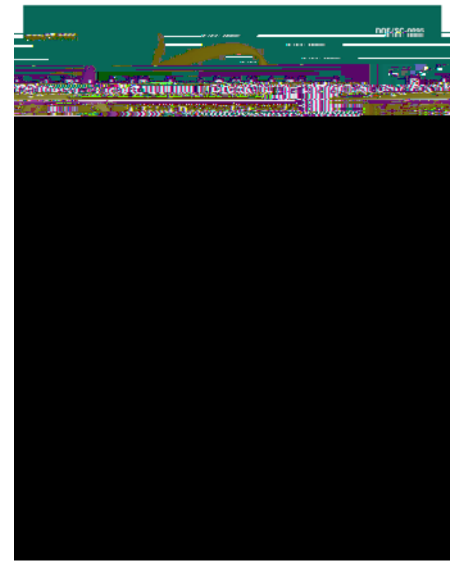

Agricultural
land
Agricultural
land
Biofuel

World bioenergy technical potential in 2050



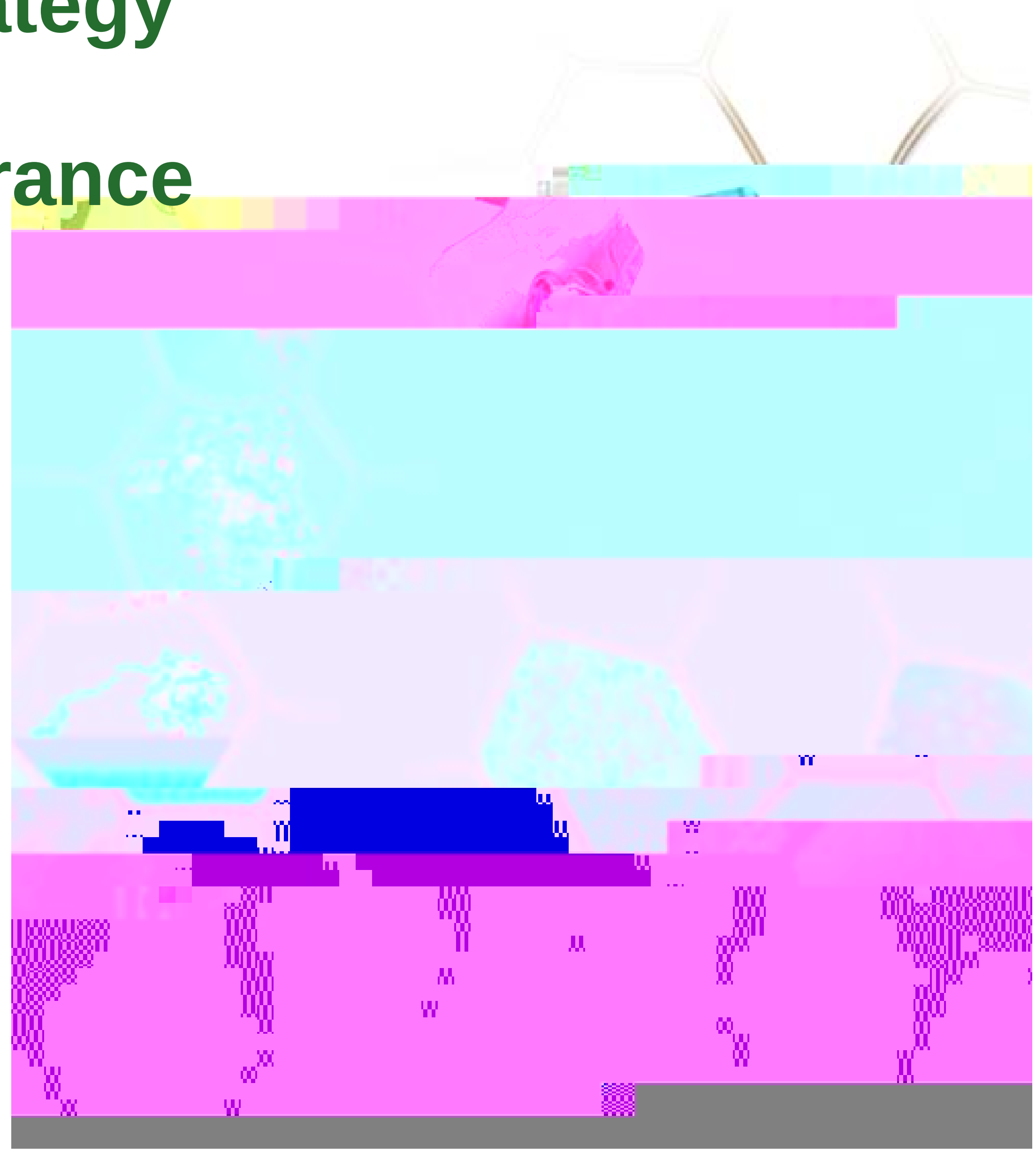
Scientific bottlenecks as of 2006

- With a deeper understanding of:
  - The resistance of lignocellulosic biomass to deconstruction
  - The genetic controls of plant composition and ultrastructure
  - Bioenergy crop domestication and sustainability
  - The structure and function of cellulases and other plant cell wall depolymerizing enzymes
  - The microbial cell's mechanisms for toxicity response
- We could envision:
  - Dedicated bioenergy crops
  - Consolidated bioprocessing – cellulase production and ethanol fermentation combined
  - Beyond "ethanol" to advanced biofuels
  - Improved pretreatments



DOE Biomass to Biofuels Workshop (12/2005)
Roadmap (7/2006)
http://doegenomestolife.org/biofuels/b2bworkshop.shtml

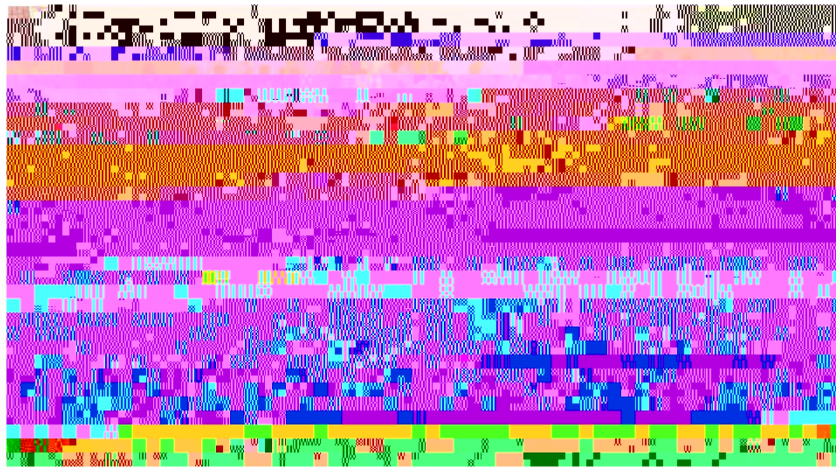
BioEnergy Science Center:
An Integrated Strategy to Understand Biomass Recalcitrance



www.bioenergycenter.org

BioEnergy Science Center (BESC)

A multi-institutional, DOE-funded center performing basic and applied science dedicated to understanding biomass recalcitrance and improving yields of biofuels from cellulosic biomass



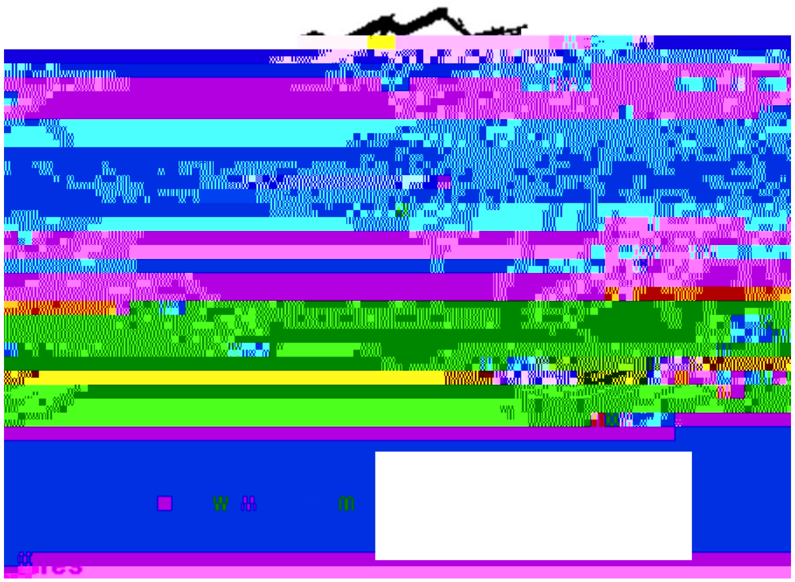
600+ People in 17 Institutions

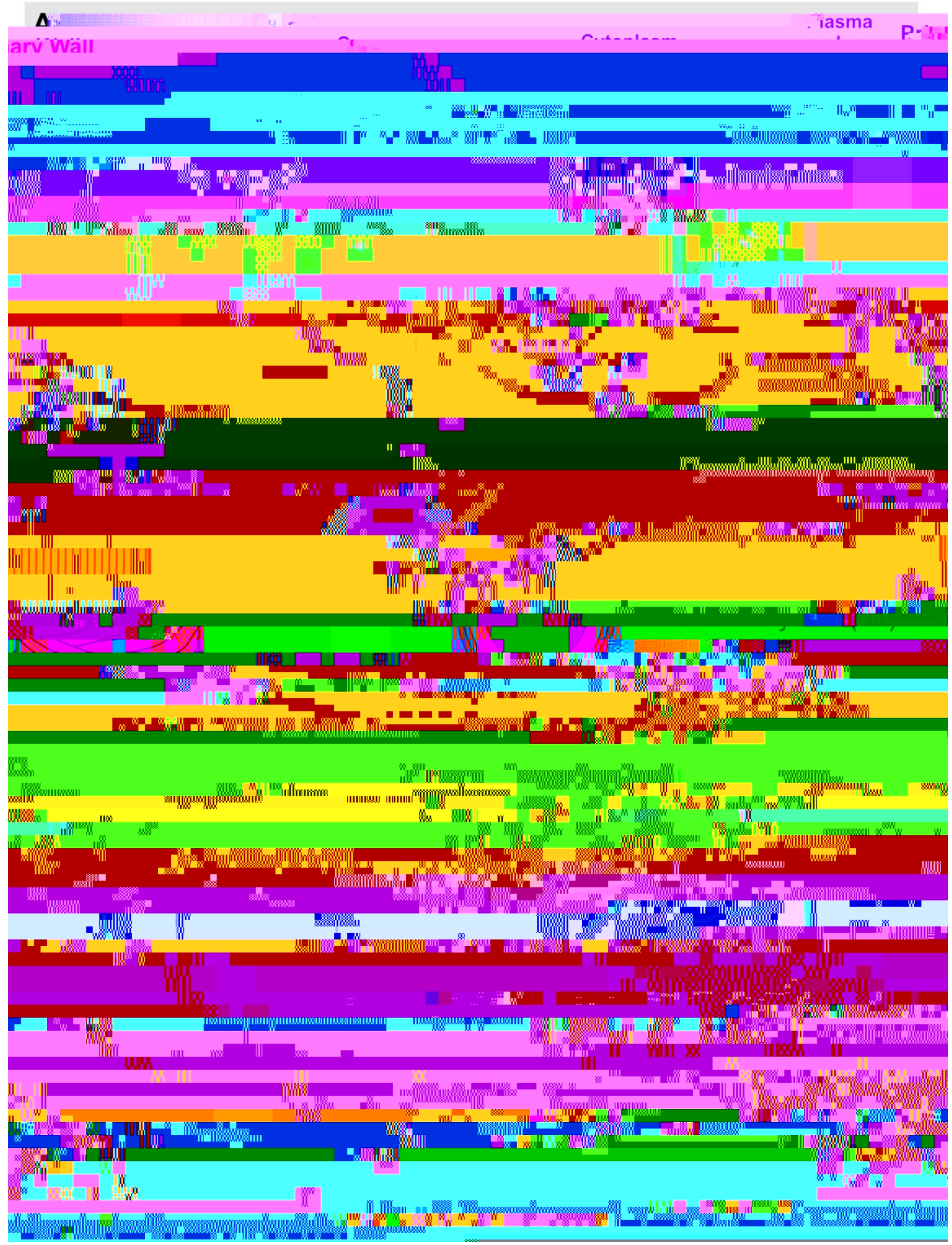
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Samuel Roberts Noble Foundation
- ArborGen, LLD
- Ceres, Incorporated
- Mascoma Corporation
- DuPont
- GreenWood Resources

- University of Georgia
- University of Tennessee
- Cornell University
- Dartmouth College
- West Virginia University
- Georgia Institute of Technology
- ersity of California--Riverside
- orth Carolina State University
- ty of California—Los Angeles

www.bioenergycenter.org

The challenges: Lignocellulosic biomass is complex and heterogeneous

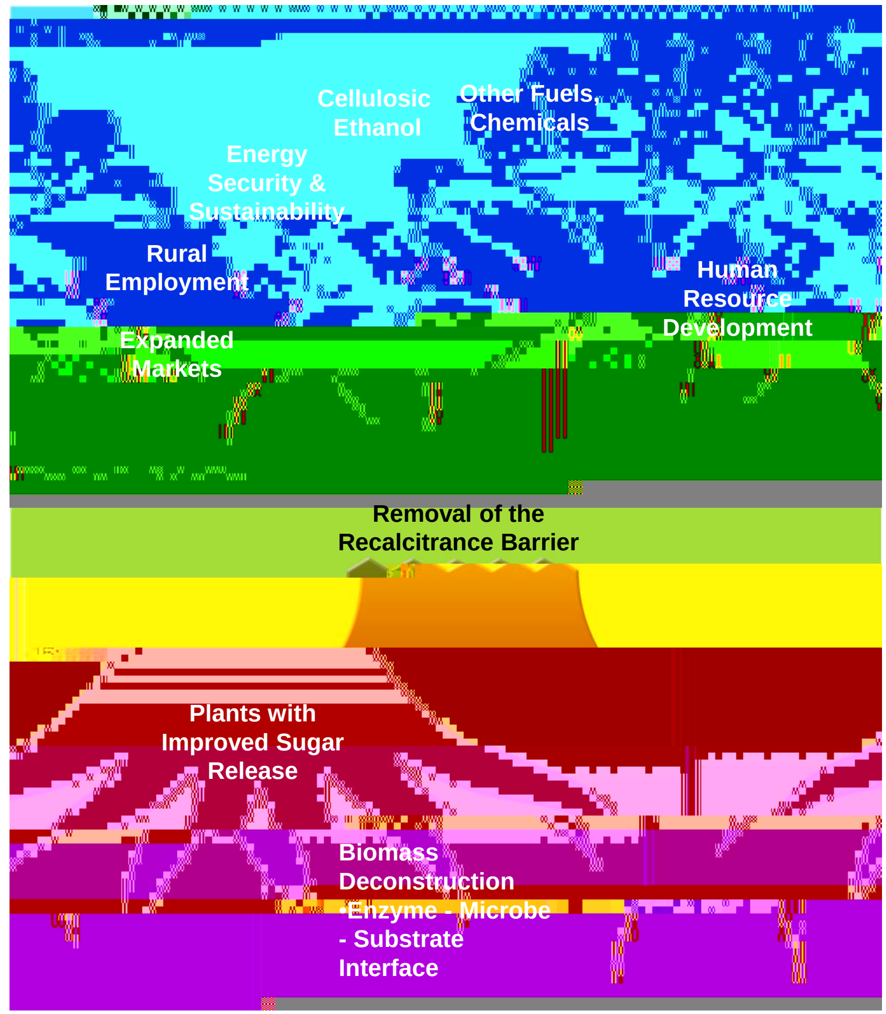




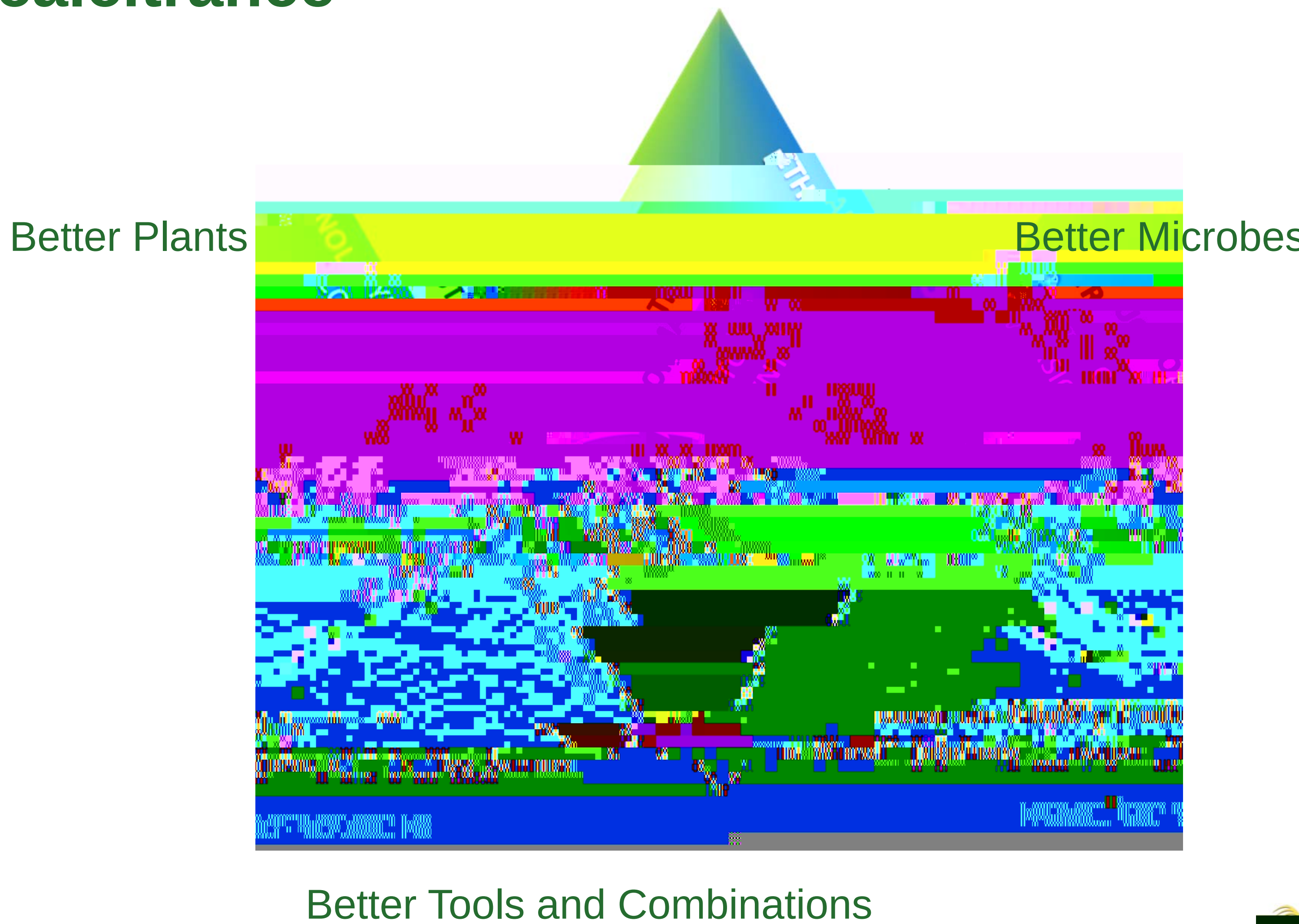
- Overcoming this recalcitrance barrier will cut processing costs significantly and be used in most conversion processes.

- This requires an integrated, multi-disciplinary approach.

- ***BESC believes biotechnology-intensive solutions offer greatest potential.***

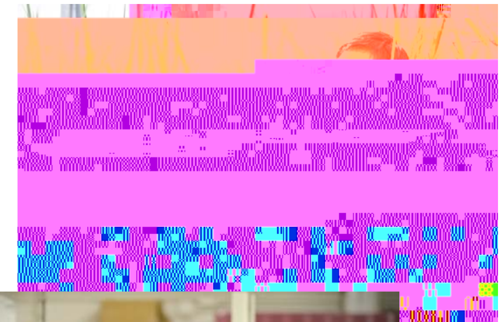


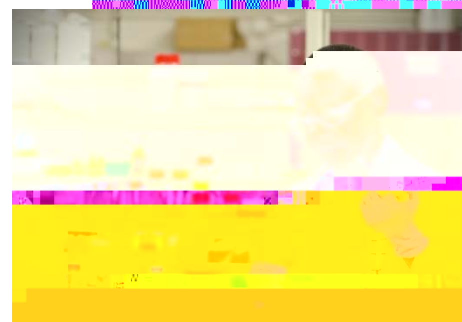
BESC is organized into three focus areas to understand biomass recalcitrance

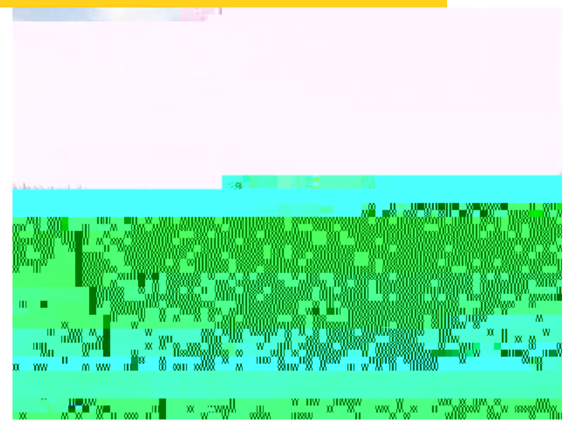


Feedstocks: then and now

Where we started	Where we are today
Lignin and cellulose accessibility believed to be the primary roots of recalcitrance	The four major wall polymers (cellulose, lignin, hemicellulose and pectin) contribute to reduced biomass recalcitrance
Low transformation efficiencies for switchgrass	Developed and utilized high (90%) efficiencies for switchgrass
Range of natural variation and genetic control of recalcitrance within a species not established	Most comprehensive systems-biology study of *Populus* and switchgrass natural variance
Natural or transgenic reduced recalcitrance perennials not available	Field trials of BESC TOP lines reveal robust reduced recalcitrance phenotypes and agronomic performance



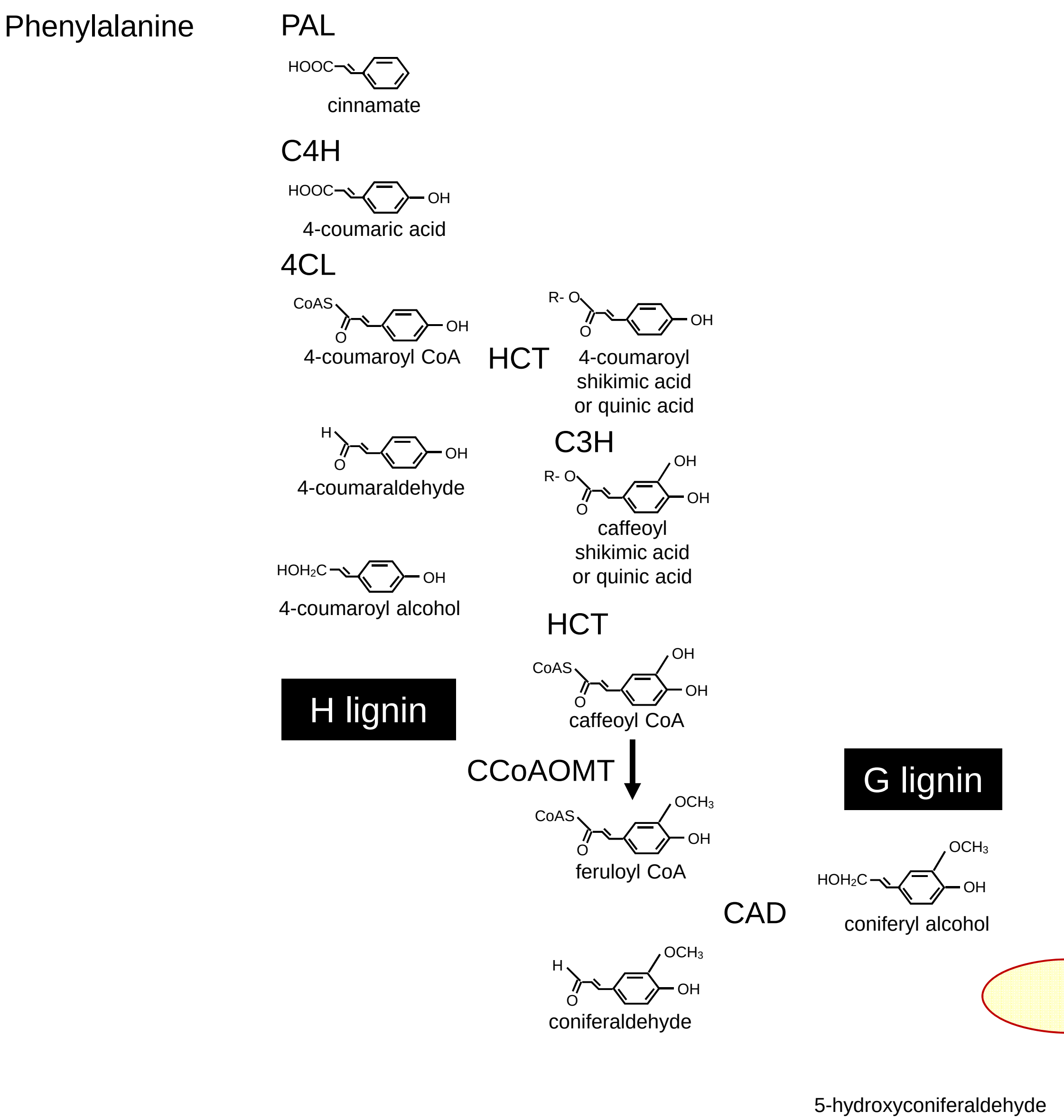




Microbial deconstruction: then and now

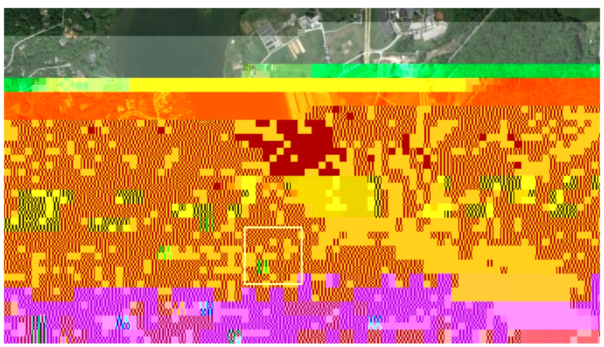
Where we started	Where we are today
Processes envisioned based on fungal cellulases	*C. thermocellum* demonstrably better than industry-standard fungal cellulase
Aggressive thermochemical pretreatment thought to be universally required	Data and analysis supporting the potential for processing with little or no thermochemical pretreatment
Functional genetic systems for cellulolytic anaerobes not described	Genetic tools developed for both *C. thermocellum* and *Caldicellulosiruptor*; systematized, higher throughput genetic system development can be envisioned
Recombinant microbes not used in the biofuel industry	

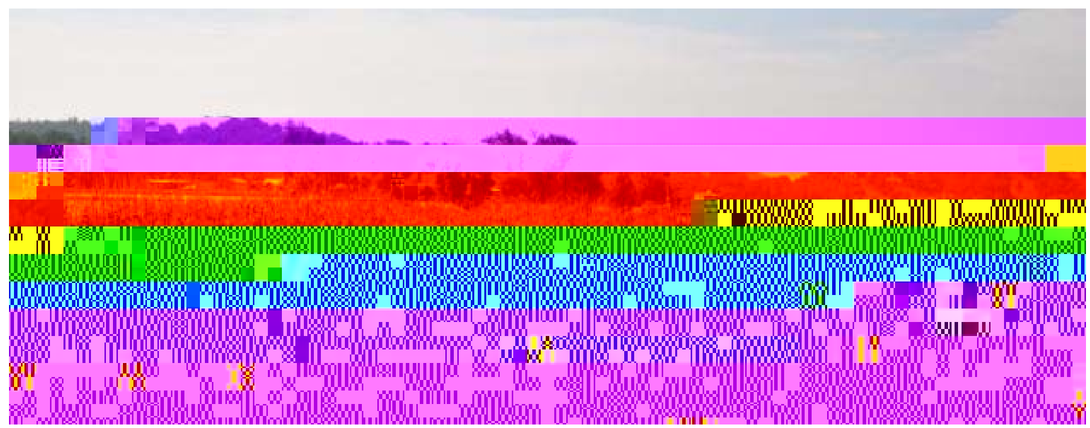
Enabling technologies: then and now


Phenylalanine
PAL
HOOC
cinnamate
C4H
HOOC
OH
4-coumaric acid
4CL
CoAS
O
OH
4-coumaroyl CoA
HCT
R- O
O
OH
4-coumaroyl shikimic acid or quinic acid
H
O
OH
4-coumaraldehyde
C3H
OH
R- O
O
OH
caffeoyl shikimic acid or quinic acid
HOH2C
OH
4-coumaroyl alcohol
HCT
OH
CoAS
O
OH
caffeoyl CoA
H lignin
CCoAOMT
OCH3
CoAS
O
OH
feruloyl CoA
G lignin
OCH3
HOH2C
OH
coniferyl alcohol
CAD
OCH3
H
O
OH
coniferaldehyde
5-hydroxyconiferaldehyde

Top performing transgenic greenhouse plants must be evaluated in the field

- Greenhouse plants have minimal stresses
- The stresses in a field may result in plants responding differently
- First year field-grown data is qualitatively consistent and second-year field grown data is better





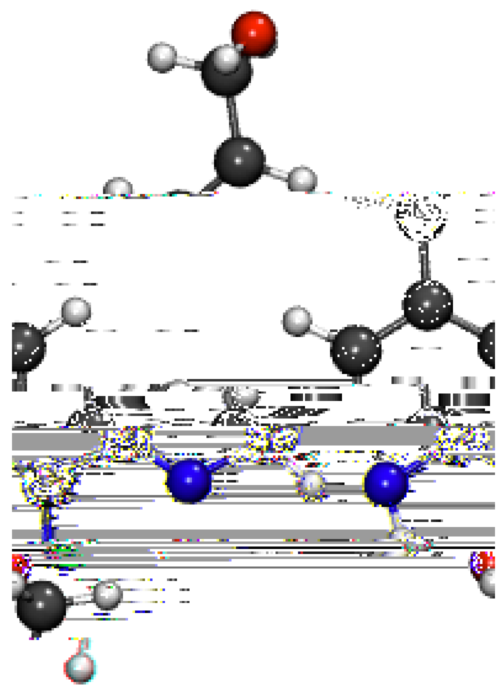
Comparison of Fermentation of Transgenic and Control SWG by Three CBP Bacteria

- Fermentation Conditions:
  - *C. obsidiansis* and *C. bescii*
    - 75 ° C and 125 rpm
  - *C. thermocellum*C. obsidiansis

New Lignol Molecule Found in COMT TG SWG Extracts

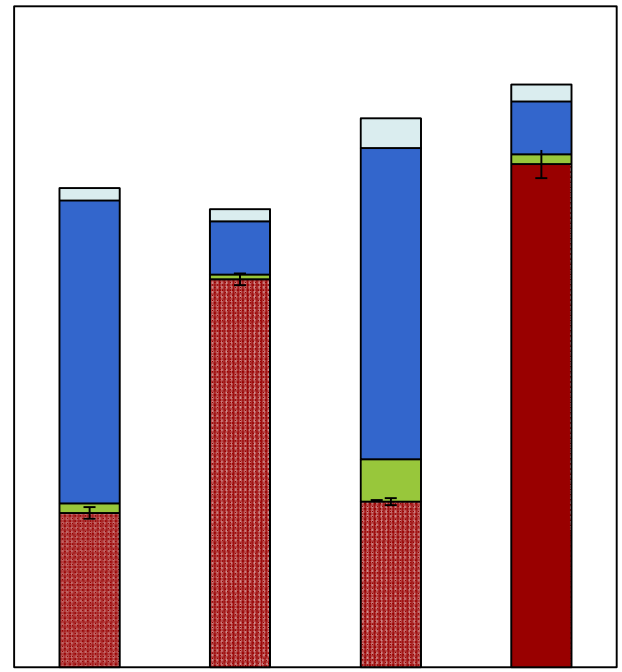
- GC-MS detected numerous compounds including a newly identified isosinapyl alcohol, preferentially in the COMT TG lines
- Identity confirmed by chemical synthesis and analysis
- Isosinapyl alcohol was determined to have mild inhibitory properties toward yeast and *E. coli*.

Sinapyl alcohol



Isosinapyl alcohol

Tschaplinski et al., 2012



Conversion (mg/g glucan loaded) for *C. thermocellum* mutant M1570 and wild-type DSM 1313 strains on both transgenic (T1-3-TG) and wild-type (T1-3-WT) switchgrass, which were pretreated with dilute acid. The standard deviation is from the average of triplicate buffered serum bottle fermentations.

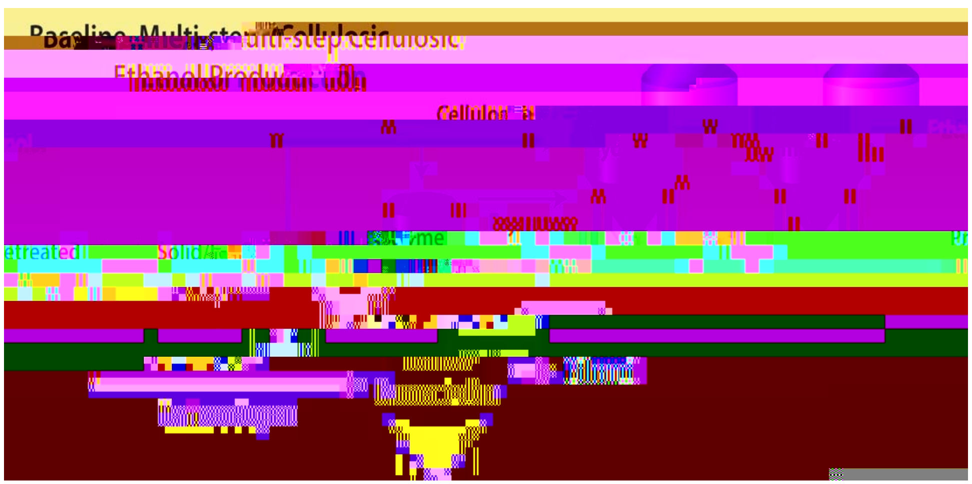
Yee *et al.*, *Biotechnology for Biofuels* 7:75, 2014.

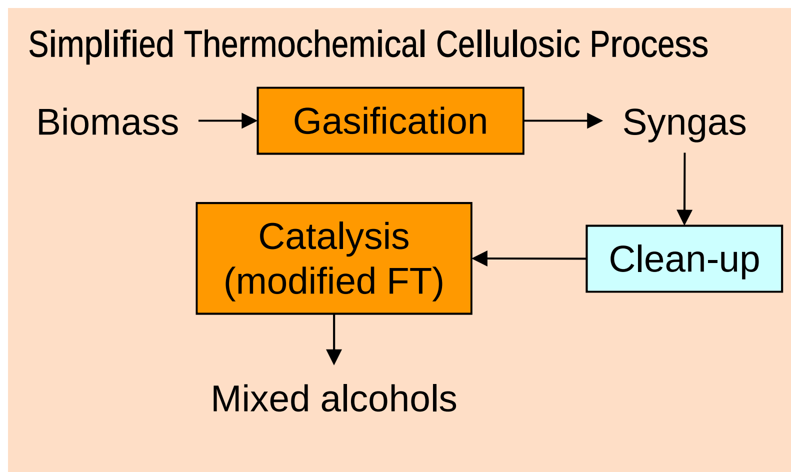
Replacing the Whole Barrel

- Cellulosic ethanol only displaces gasoline fraction of a barrel of oil (about 40%)
- Reducing dependence on oil requires replacing diesel, jet, heavy distillates, and a range of other chemicals and products
- Greater focus needed on RDD&D for a range of technologies to produce hydrocarbon fuels and displace the entire barrel of petroleum

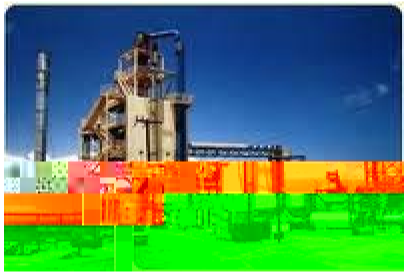
Cellulosic Conversion Improvement Strategies

- State of art versus theory
  - Biological has lower theoretical yield (~100 gal/ton) but higher achieved yields (70-85 gal/ton) and potential co-products
  - Thermochemical has highest theoretical yield (~120+ gal/ton) but much lower achieved yield (50-65 gal/ton) and less desirable coproducts (i.e., methanol)

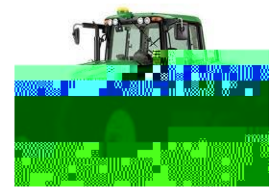


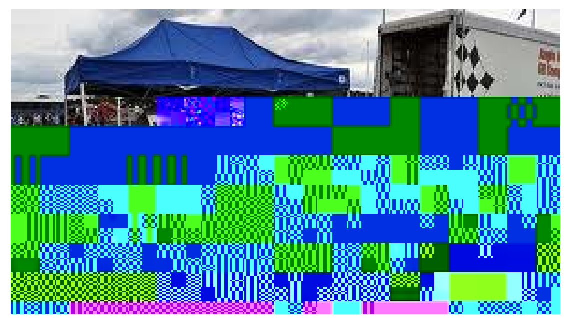


Technology - A general platform for converting fermentation streams to hydrocarbon blend-stock



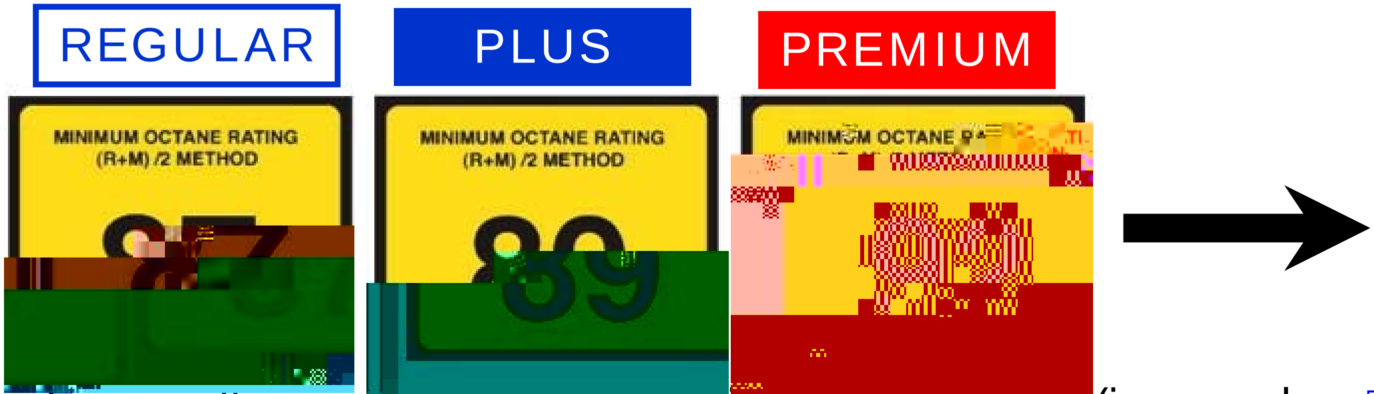
Fermentation stream or distilled alcohol → Catalyst → Blend-stock +Water + VOC

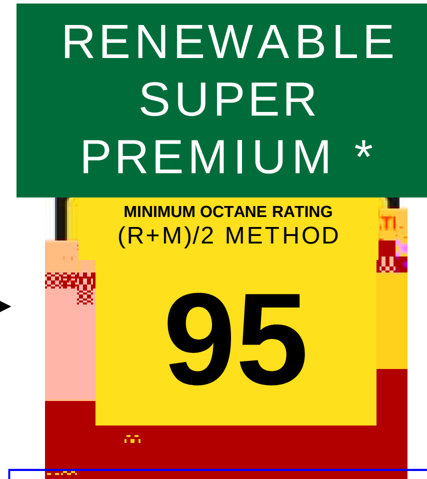




Catalytic ethanol upgrading into

Is a “Renewable Super Premium”* a better path for ethanol?





- Engine efficiency can improve with increasing ethanol (in properly designed future engines/vehicles)
  - Chemical octane number + latent heat of vaporization permit higher compression ratio, optimized combustion phasing, increased power (downspeeding/downsizing)
- Likely that optimum blend is ~E20-E40
  - Energy density penalty is *linear* with ethanol concentration, power and efficiency gains are *non-linear*
  - Tradeoff in efficiency, cost, and fuel economy
  - Ideal blend in <u>optimized</u> vehicles could improve fuel economy while using more ethanol
  - Also legal to use in ~16M legacy FFVs

* “*Renewable Super Premium*,”
“New regular,”
“High Octane Base Fuel…”
Regardless of name, high octane blends have significant potential

Advanced biotechnology game-changers to be monitored

- Parallel improvement of yield and convertibility in biofeedstocks and residues
- Robust easily convertible lignocellulosic feedstocks and residues with minimal pretreatment
- Rational agronomic improvements of feedstocks for yield and sustainability (such as low nitrogen and water use and increase soil organic carbon fixation).
- Ability to control the rhizosphere (the soil microbial communities) to improve biofeedstock traits
- Economic stable bioconversions able to handle biofeedstock variability
- New tools to rapidly and rationally genetically engineer new microbial isolates with unique complex capabilities (such as for new enzymes, fuels, or products or for harsh conditions such as pH or temperature)
- Rational reproducible control of carbon and energy flux in microbes (such as decoupling growth from metabolism)
- Ability and understanding to reproducibly overcome fermentation product inhibition by cellular redesign while maintaining yield and rate.
- Stable high rate microalga lipid production in open systems
- Expanded compatible biotechnology processes to co-products while producing fuels-such as from lignin.

Davison et al., 2015. "The impact of biotechnological advances on the future of U.S. bioenergy," *Biofuels, Bioprod. Biorefin.* 9:454 (2015).

Science and Technology are critical but policy is also important

- Active policy debates on
  - Sustainability
    - Life cycle assessments - LCA (carbon, water and energy balances)
    - Land-use change (LUC) and indirect land-use change (ILUC)
  - Food vs. fuels
  - The "Blend Wall"
    - How much ethanol can go into gasoline in typical engines?
    - Market is almost saturated with E10 in U.S.
  - Fungible or "drop-in" fuels
- Externalities on
  - Capital and financing
    - Estimate EISA goal will require 100-300 biorefineries of 50-100M gal/y in US
  - Feedstock deployment and agriculture incentives

Challenges

- U.S. - The growing schism between climate and energy security communities will delay deployment
  –

Bioenergy scientists need to respond to our publics

- Arm yourself with knowledgeable talking points; example
- *Nature Climate Change* April 2014 Liska et al.
  - "Biofuels from crop residues can reduce oil carbon and increase CO2 emissions"
  - Washington Post: **"Biofuels worse than gasoline"**

- Assumes:
  - 75% of stover removed
  - Ignore use of lignin for fuels
  - Not based or compared to best current models that account for management and are in RFS

- Consensus
  - most farmers and studies only remove <25%
  - Current and future cellulosic biorefineries use lignin for heat and power
  - EPIC, GREET

Farming for Fuels lessons reach thousands of students through hands-on science activities

- BESC in collaboration with the Creative Discovery Museum (CDM) in Chattanooga, Tennessee, developed hands-on lesson plans for students in 4th, 5

Acknowledgements

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BESC Collaborators:

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NREL: Rob Sykes, Mark Davis, Erica Gjersing
Noble/UNTexas: Rick Dixon, C. Fu
UTK: Neal Stewart, H Baxter, M. Mitra
Outreach: Jan Westpheling (UGA), Wayne Robinson (CDM)

Biofuels:

UTK: Art Ragauskas,
ORNL: Tim Theiss, Virginia Dale, Keith Kline, Chaitanya Narula,