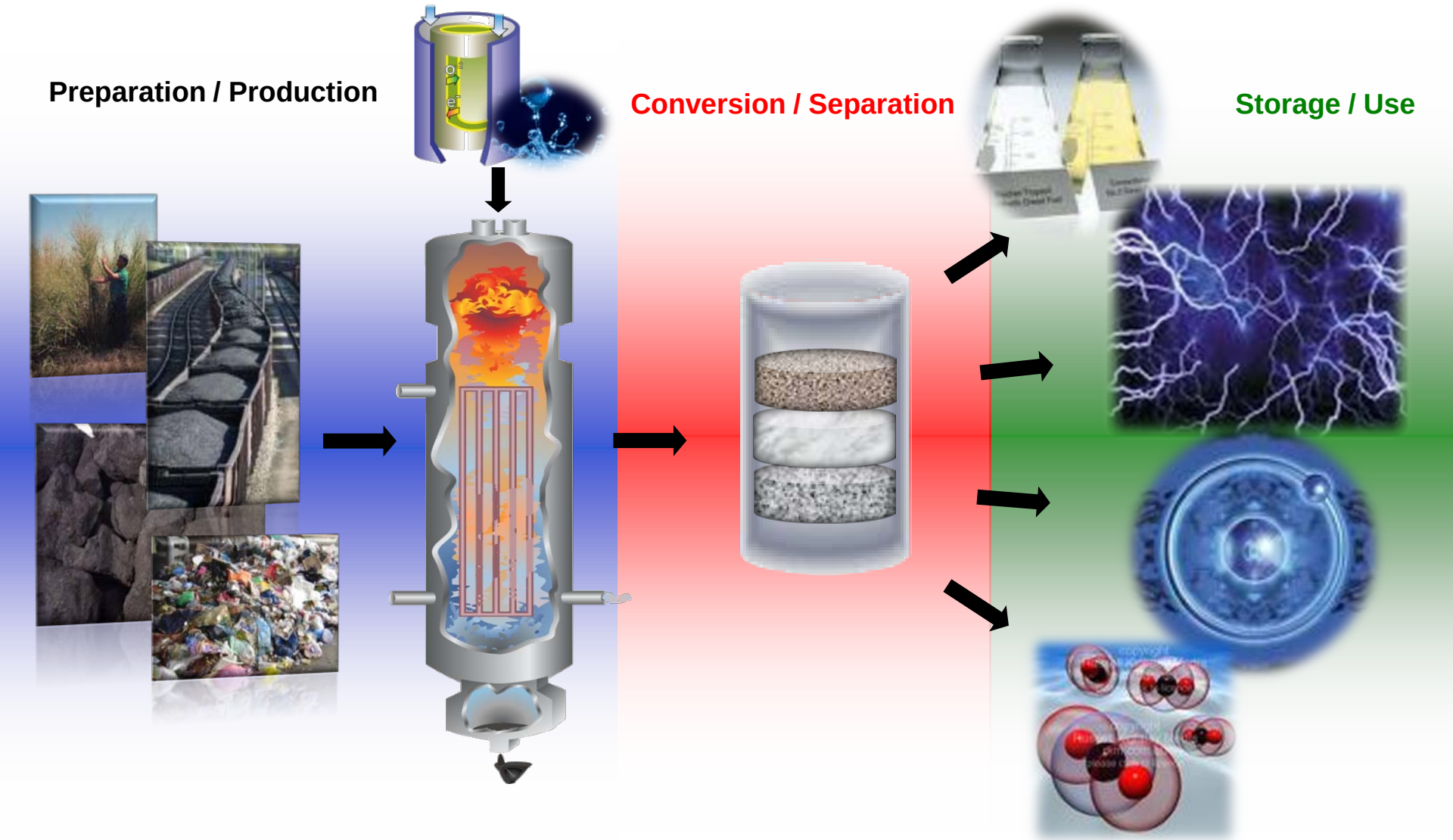
NATIONAL ENERGY TECHNOLOGY LABORATORY

Development of Secure and Clean Energy Technologies: Co-gasification

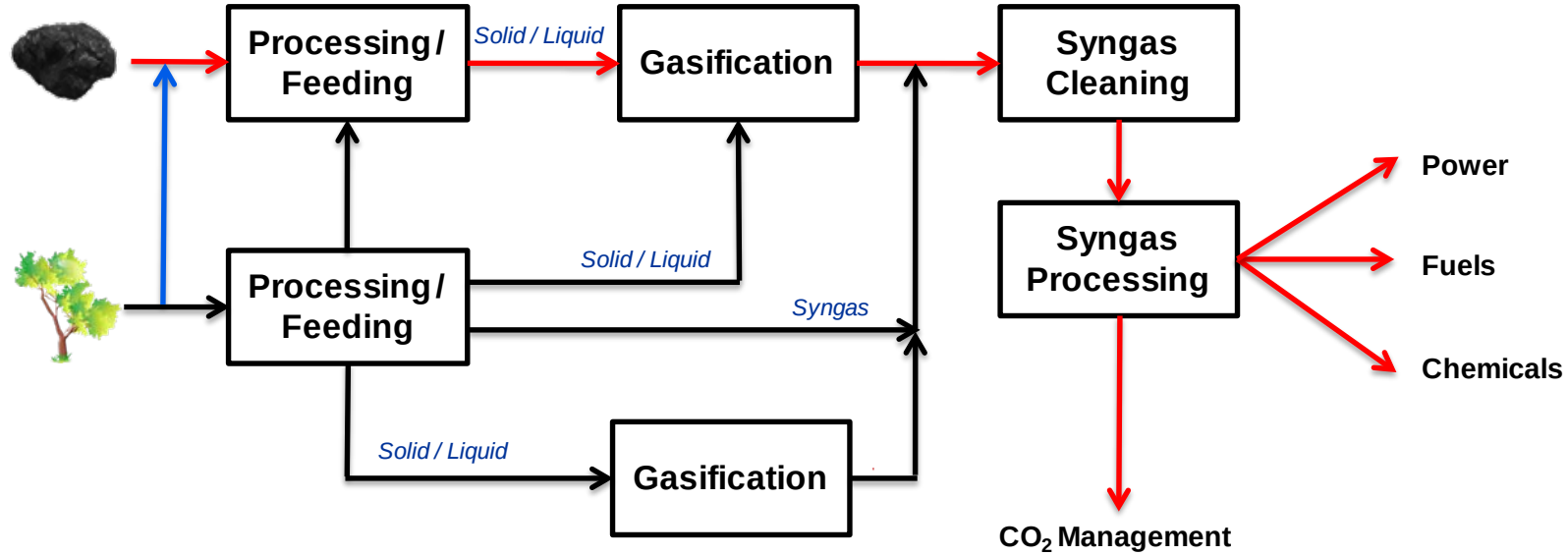
Reaction Chemistry & Engineering Group

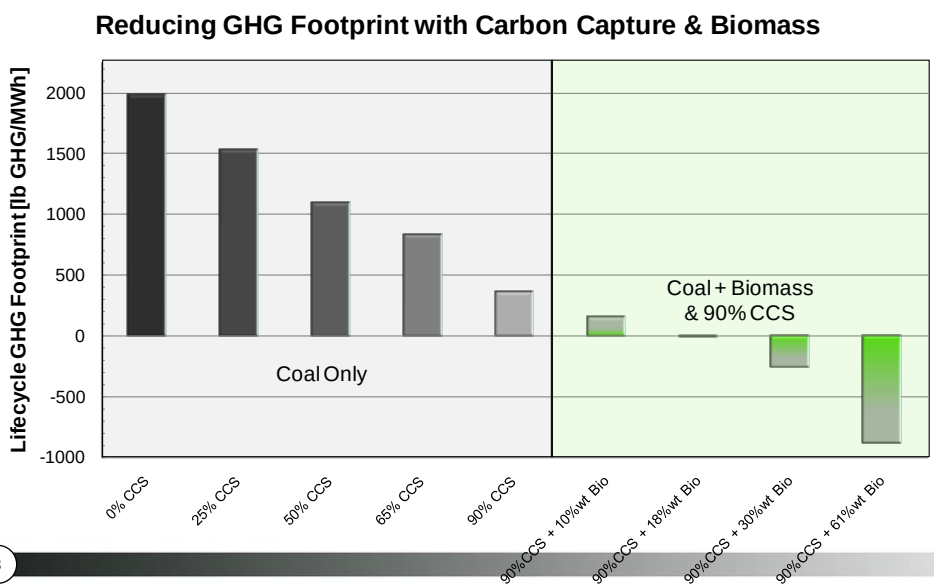
January 25, 2010

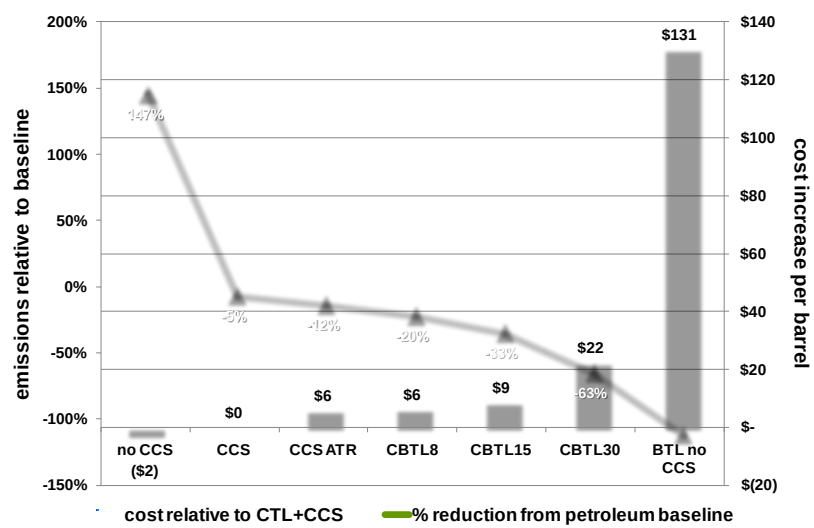
Research Path Towards Nationally Secure Energy



Coal Utilization with Environmental Mitigation:
Systems Analysis and Process Optimization



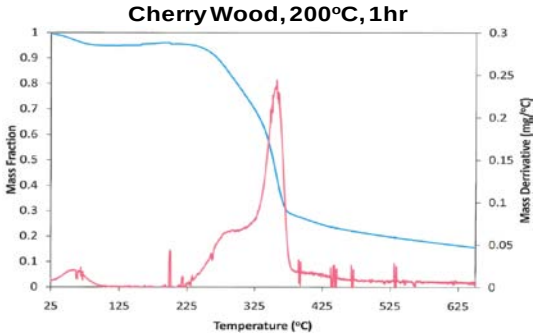




•NETL Office of Systems, Analysis and Planning

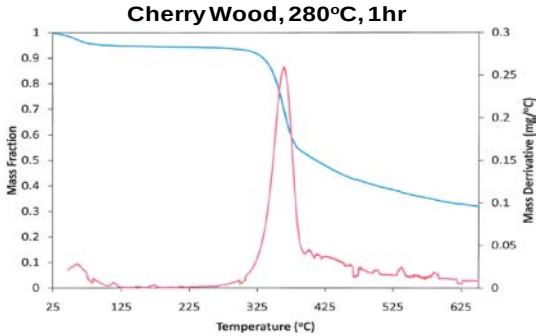
Co-gasification: Pretreatment of Biomass

- **Goal:**
  - Identify optimum pretreatment methodology for co-feeding biomass with coal
- **Approach:**
  - Mild thermal treatments, such as torrefaction, can significantly impact the mechanical characteristics of biomass
  - Appropriate pre-treatment could allow biomass to be fed seamlessly with current coal gasification systems



Before and After Grinding for 6 min in a 3" Ball Mill

Young's Modulus = 1.63 +/- 0.26



Before and After Grinding for 6 min in a 3" Ball Mill

Young's Modulus = 0.67 +/- 0.21

Co-gasification: Rate and Production Effects

Goal

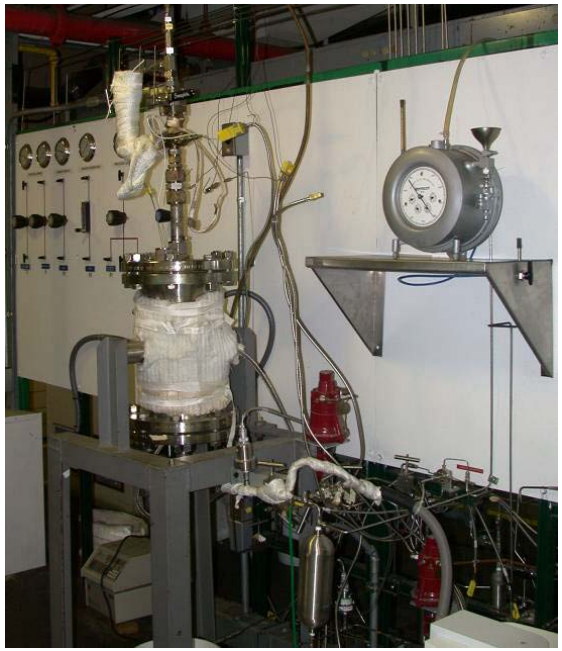
- Develop an understanding of the influence of coal and biomass mixtures on gasification related reactions as well as gaseous, liquid and solid products

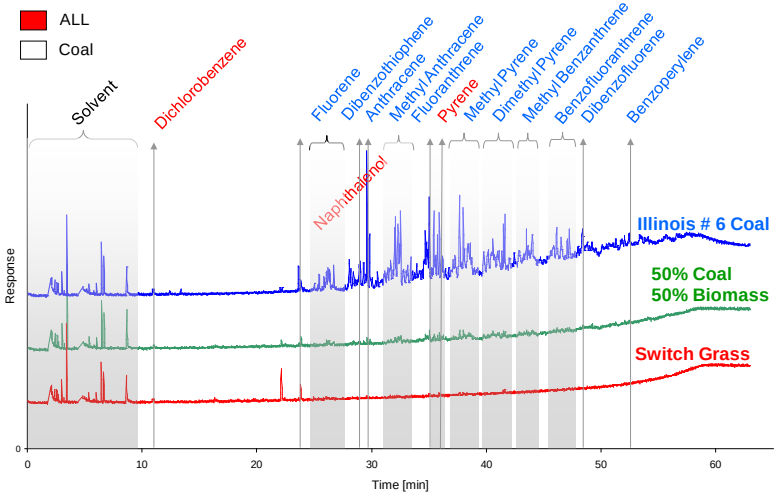
Specific project objectives

- Conduct batch tests on pyrolysis and gasification reactions using various coal and biomass types and ratios

  Coal: Illinois #6, Wyodak, Powder River Basin, North Dakota Lignite

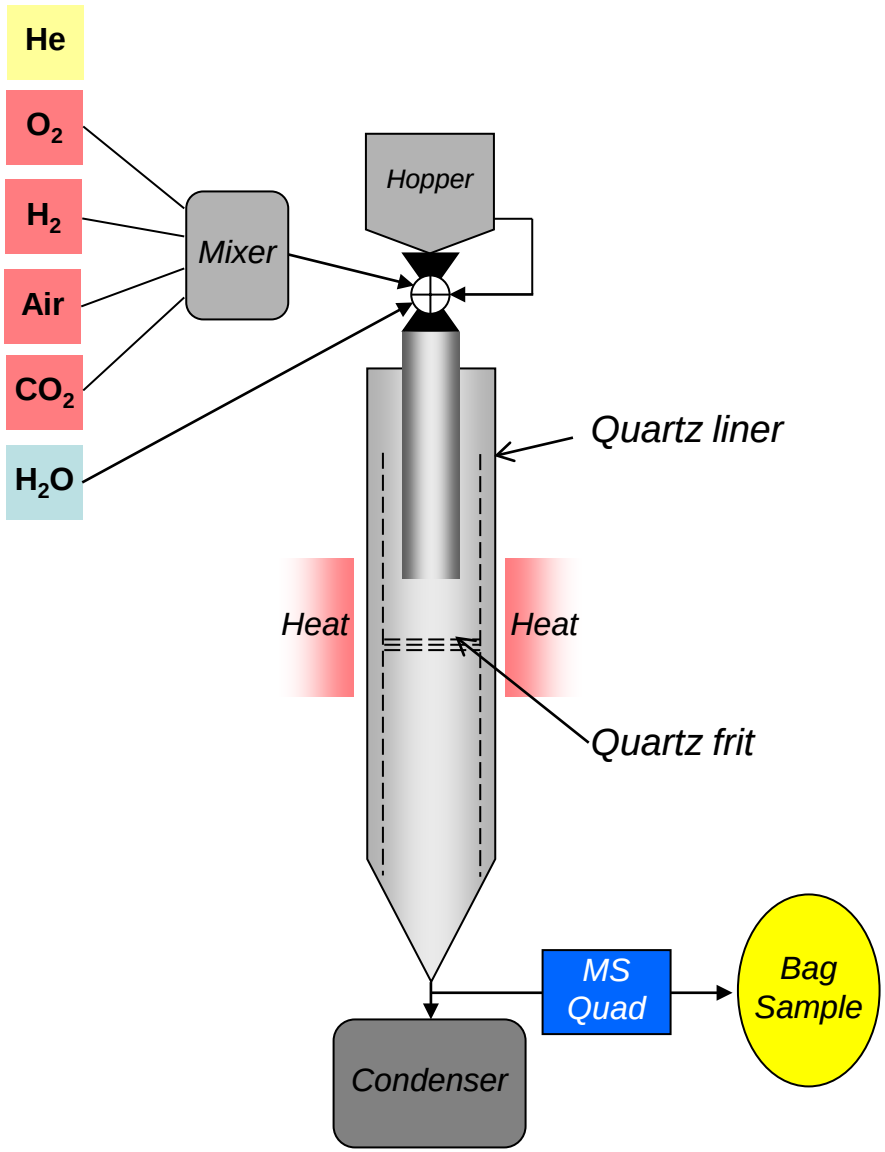
  Biomass: Mixed hardwood, Wheat straw, Corn stover, Switchgrass, DDG with corn fiber, Algae
- Develop kinetic expressions for gasification related reactions based on feed composition
- Conduct thorough chemical analysis on products resulting from gasification reactions
  - On-line quadrupole mass spec
  - Off-line GC-MS of tars and chars





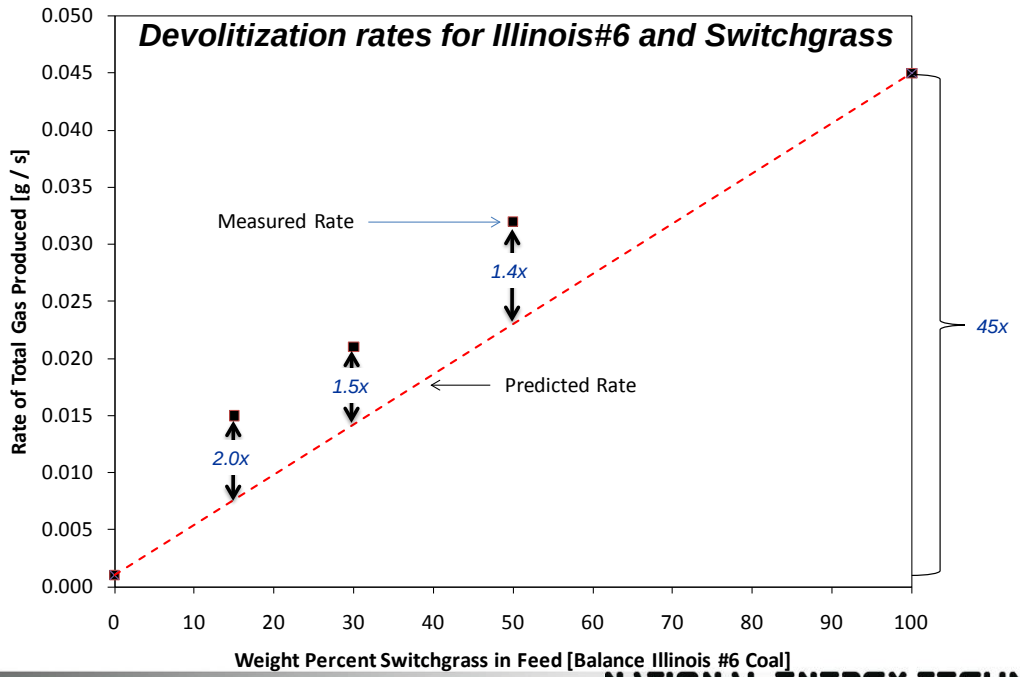
Batch Gasifier: Experimental Set-up

- **Reactor and conditions**
  - Batch mode
  - Up to 1000 °C, 1000 psi
- **Pre-mixed coal:biomass samples**
  - 100, 75, 50, 25, 0 wt% coal
  - balance is biomass
- **Coal types**
  - Illinois #6
  - Wyodak
  - Powder River Basin
  - North Dakota Lignite
- **Biomass types**
  - Mixed hardwood
  - Corn stover
  - Switchgrass
  - DDG with corn fiber
  - Algae



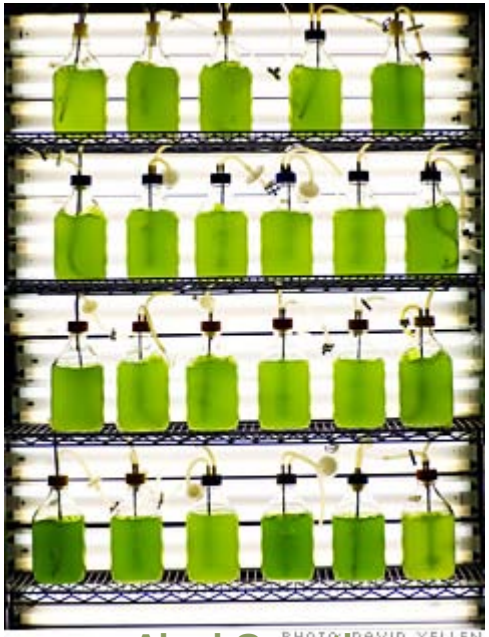
Co-gasification: Rate and Production Effects

- **Gasification reaction chemistry**
  - The addition of biomass appears to increase both the rate and extent of gasification reactions
    - Rate increases as high as 2x
    - Possibly due to catalytic activity of char or high O_2 content of biomass
  - Gaseous and condensed products:
    - Coal-rich feeds show more S-containing compounds
    - Biomass-rich feeds show more O-containing compounds



Algae-based Carbon Capture
What is it?

- **Process to capture fossil fuel-derived CO_2 with controlled biomass growth**
- **Carbon Recycling (capture and reuse) – *Not* Sequestration**
  - Does <u>not permanently remove</u> CO_2 from the air
  - Can re-use power plant CO_2 (burn it twice)
- **Makes useful by-products (bio-fuels)**
  - Potential to produce specific fuels and chemicals
  - Increased energy security – displaces imported petroleum with domestic resource



•**Algal Growth**

•*Photo:* Fortune Magazine (April, 2008)

- **Can reduce carbon footprint of fossil power plants**
  - Can use CO_2 from combustors or gasifiers
  - May have some power plant applications (if it can be competitive with geologic CCS on $/ton)

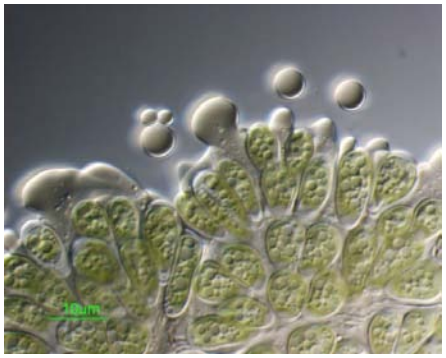
Advantages of Algae as Fuel Precursor

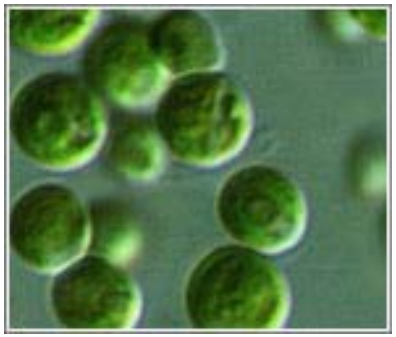
- **Algae growth**
  - Extremely rapid growth potential – some species double in 24 hrs
  - Able to grow in unconventional scenarios – lessens “food for fuel” debate
  - Utilize CO_2 – could offset emissions
  - Produce relatively high concentrations of bio-oil (lipid)
- **Routes to fuels**
  - Chemical transformation of algae lipids
    - Extraction, conversion
    - Residue available for further processing
  - Biomass gasification
- **NETL in-house efforts are directed toward three pathways**
  - Accurate assessment of lipid production and composition
  - Alternative oil conversion pathways to achieve alkane-based fuel
  - Growth and response studies in presence of flue gas contaminants

Algae Growth for Fuel Production

Specific project objectives

- Growth:
  - Identify the impact of flue and syngas contaminant as well as environmental conditions on algal growth and lipid content
- Extraction:
  - Develop efficient extraction methods for the isolation of lipids from algae
- Gasification:
  - Identify the influence of co-feeding on gasification chemistry
- Fuels:
  - Develop methods for conversion of algae lipids into alkane-based liquid fuels
    - Compatible with existing infrastructure
    - Avoid potential performance issues with methyl-ester based biofuels

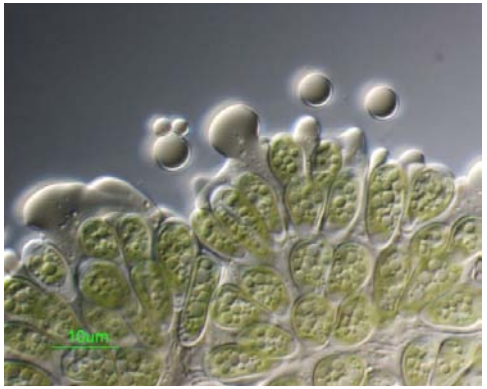




Algae Growth and Response Studies

- **Initial Species for Growth Studies**
  - Chlorella vulgaris
    - Robust grower, outcompetes other strains in mixed-culture scenarios
    - Produces “typical” lipid inside cell wall, composed of fatty acids and glycerides
  - Botryococcus braunii
    - Excretes a hydrocarbon-based lipid (isoprene)
- **Goals**
  - Provide baseline data on “pure” streams
  - Identify and induce appropriate alterations/stresses in system
    - Light levels
    - NO_x, SO_x
    - Nutrient levels
  - Determine growth, lipid production, contaminant fate & transport
  - Incorporate algae as biomass feedstock

•Chlorella vulgaris, image by jash botanicals



•Botryococcus braunii, image by Texas A&M

Gravimetric Lipid Determination

- **Percent lipids from SAME SPECIES**

Method	Reagents	Conditions	Wt % lipids
Bligh-Dyer	MeOH:$CHCl_3$	2:1 at 20°C	13.1 ± 1.9
Folch	MeOH:$CHCl_3$	1:2 at 20°C	20.6 ± 1.2
Markham	Hex:IPA:H_2O	(55:20:25) at 60°C	20.2 ± 1.2
Markham + HCl	Hex:IPA:H_2O + HCl	(55:20:25) at 60°C	28.0 ± 7.0
MeOH	MeOH	60°C	19.4 ± 2.1
MeOH + HCl	MeOH + HCl	60°C	27.1 ± 7.7
Guckert	Hex:IPA:H_2O	(17.5:12:0.75) at 20°C	3.6 ± 1.4
Smedes	Hex:IPA:H_2O	(8:10:11) at 20°C	6.4 ± 0.6
Fajardo	EtOH	20°C	3.0 ± 1.3
Fajardo + HCl	EtOH + HCl	20°C	11.0 ± 2.0
EtOH	EtOH	60°C	11.3 ± 3.3
EtOH + HCl	EtOH + HCl	60°C	19.7 ± 3.5
Hexane	Hexane	20°C	3.8 ± 0.8
Hexane + HCl	Hexane + HCl	60°C	16.8 ± 0.1

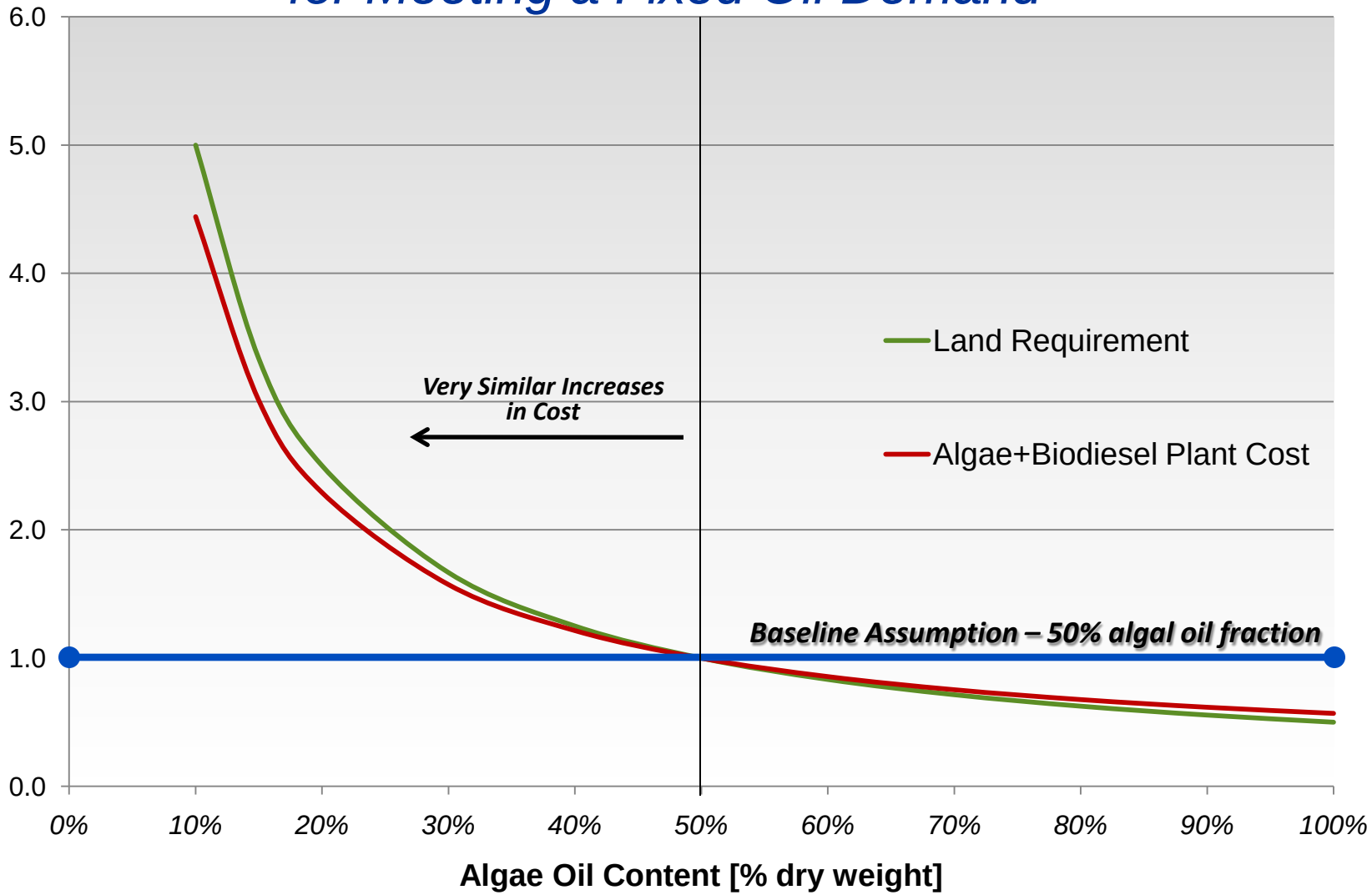
Gravimetric lipid determinations can be *inaccurate* and *misleading*

Refining the Results

Extraction Method	Raw Gravimetric % lipid (dry wt)	Direct Transesterification (GC-FID)
Scenedesmus sp.		30.4 ± 0.5
Bligh Dyer	32.5 ± 0.4	
Methanol + HCl	55.3 ± 0.9	
Hexane + HCl	7.6 ± 0.4	
NS-1		2.3 ± 0.2
Bligh Dyer	5.8 ± 1.7	
Methanol + HCl	52.0 ± 1.3	
Hexane + HCl	2.0 ± 1.0	
Chlorella vulgaris		12.6 ± 4.7
Bligh Dyer	12.5 ± 1.1	
Methanol + HCl	20.4 ± 2.9	
Hexane + HCl	1.7 ± 0.2	
Chlorella pyrenoidosa		14.1 ± 3.0
Bligh Dyer	17.2 ± 4.0	
Methanol + HCl	24.9 ± 0.7	
Hexane + HCl	4.7 ± 0.3	

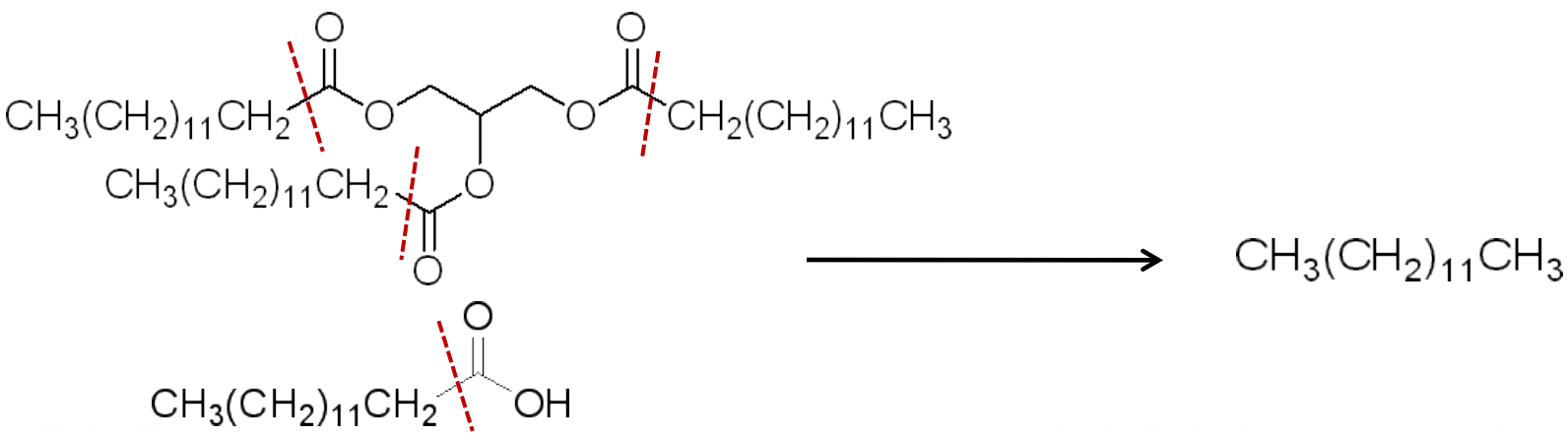
Relative Algae System Requirements –

for Meeting a Fixed Oil Demand



Algae Oil to Alkane-based Fuels

- **Conventional conversion of lipid is trans-esterification to FAME mixture**
  - So-called “biodiesel” can be blended into conventional liquid fuels
  - Highly oxygenated mixture has some undesirable properties
    - Low-temperature issues (cold flow, freeze point)
    - Water absorption issues
- **Goals**
  - Explore alternative conversion pathways to achieve a truly transparent “drop-in” fuel
  - Requires selective decarboxylation reactions



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