



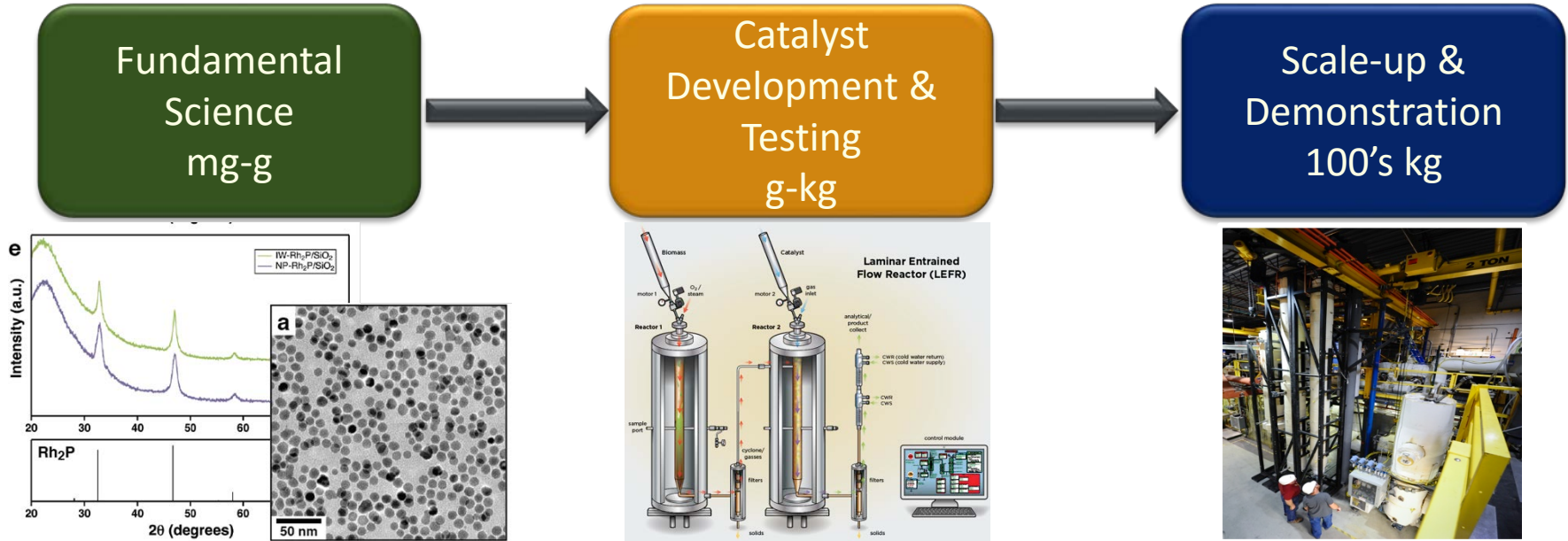
# Mass Spectrometer capabilities at NREL

Marc Pomeroy

June 10, 2016 – Gas Analysis Workshop

# Finding Solutions for Biomass Conversion at NREL

Research at multiple scales from fundamental, to bench, to pilot plant.



Overarching research necessary to support lab and industrial deployment.

Feedstocks



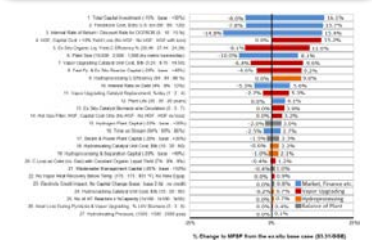
Bio-Oil  
Characterization



Gasification  
Products

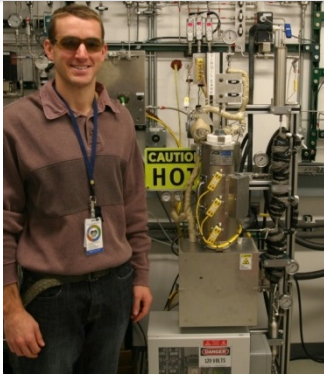


Technoeconomic  
Analysis

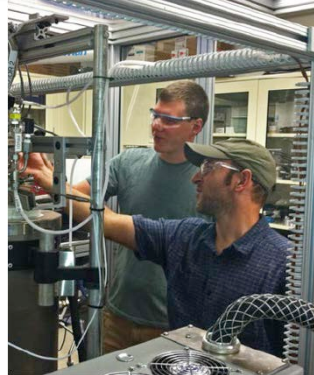


# Thermochemical platform at NREL has multiple systems from mg to 450kg/day scales and operating in a variety of configurations

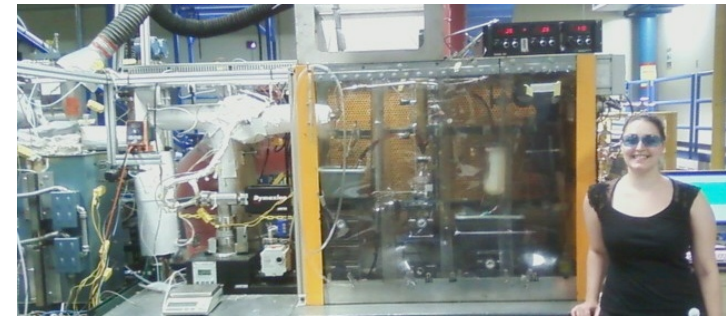
Small Scale Reactors:  
Catalyst Development  
Catalyst use per test: 0-2g



Laminar Entrained Flow  
Reactor: In-Situ Pyrolysis  
Biomass rate: <5 g/hr



2" Fluidized Bed Reactor:  
Fast, Ex-situ, & In-Situ Pyrolysis  
Biomass rate: <0.5 kg/hr



4" Fluidized Bed Reactor:  
Gasification  
Biomass rate: <2 kg/hr



Davison Circulating Riser:  
Ex-Situ Pyrolysis  
Biomass rate: <5 kg/hr



Thermochemical Process  
Development Unit: All Pathways  
Biomass rate: <30 kg/hr



# All systems are capable of hot real-time sampling



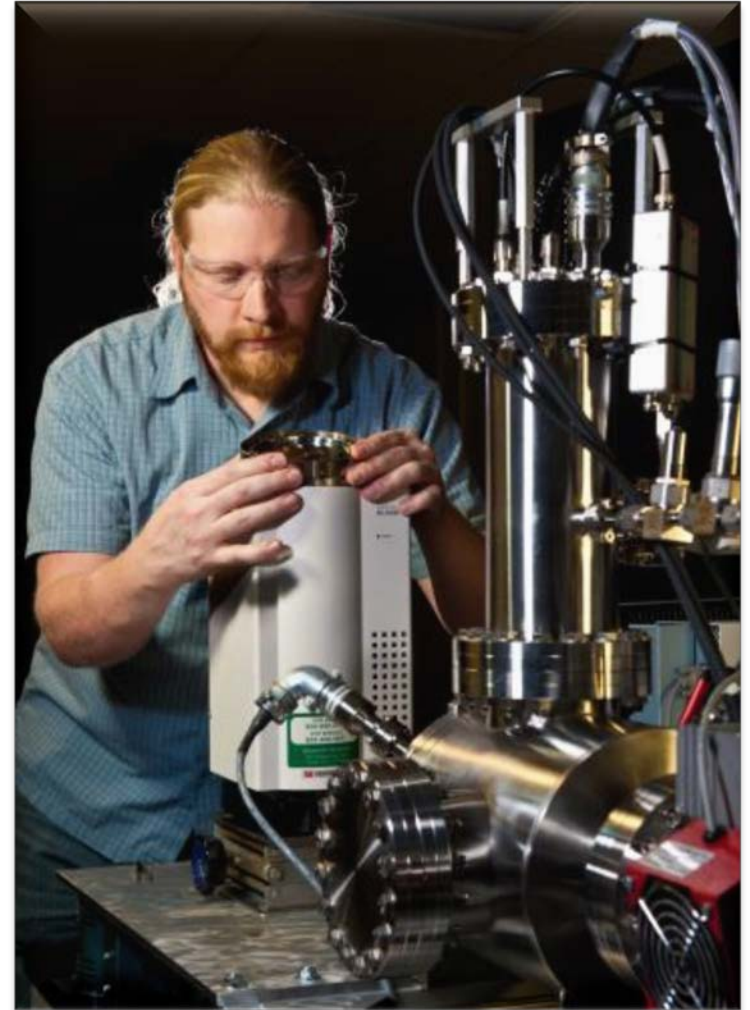
- Molecular Beam Mass Spectrometer (MBMS)
  - Sampling up to 500° C
  - Supersonic expansion, rapid cooling/rarefaction preserves sample without condensation or reaction
  - Mass analysis provides instantaneous chemical fingerprint of on-line sample

# Molecular Beam Mass Spectrometry – 6 Instruments

- 1 AMU resolution
- 0-500 AMU range
- Robust continuous online sampling of gas and condensable vapors
- EI Ionization at low voltages  $\sim 23$ -eV to minimize fragmentation
  - Results in lower ion signals
  - Loss of chemical information from overlapping of isomers
  - Non-selective ionization

# MBMS – High Throughput

- Two systems for high throughput screenings
  - Raw Biomass Pyrolysis
  - Catalytic Upgrading
  - 0-1000 AMU for these two instrument



# Triple Quad - TQMBMS



- Triple Quad for
  - Ease of reactor change for general use
  - Fragmentation studies
  - Typically small batch experiments

# Cross-Beam MBMS

- Cross-Beam
  - Higher sensitivity than linear systems
  - General use instrument
  - Small batch and continuous on-line monitoring



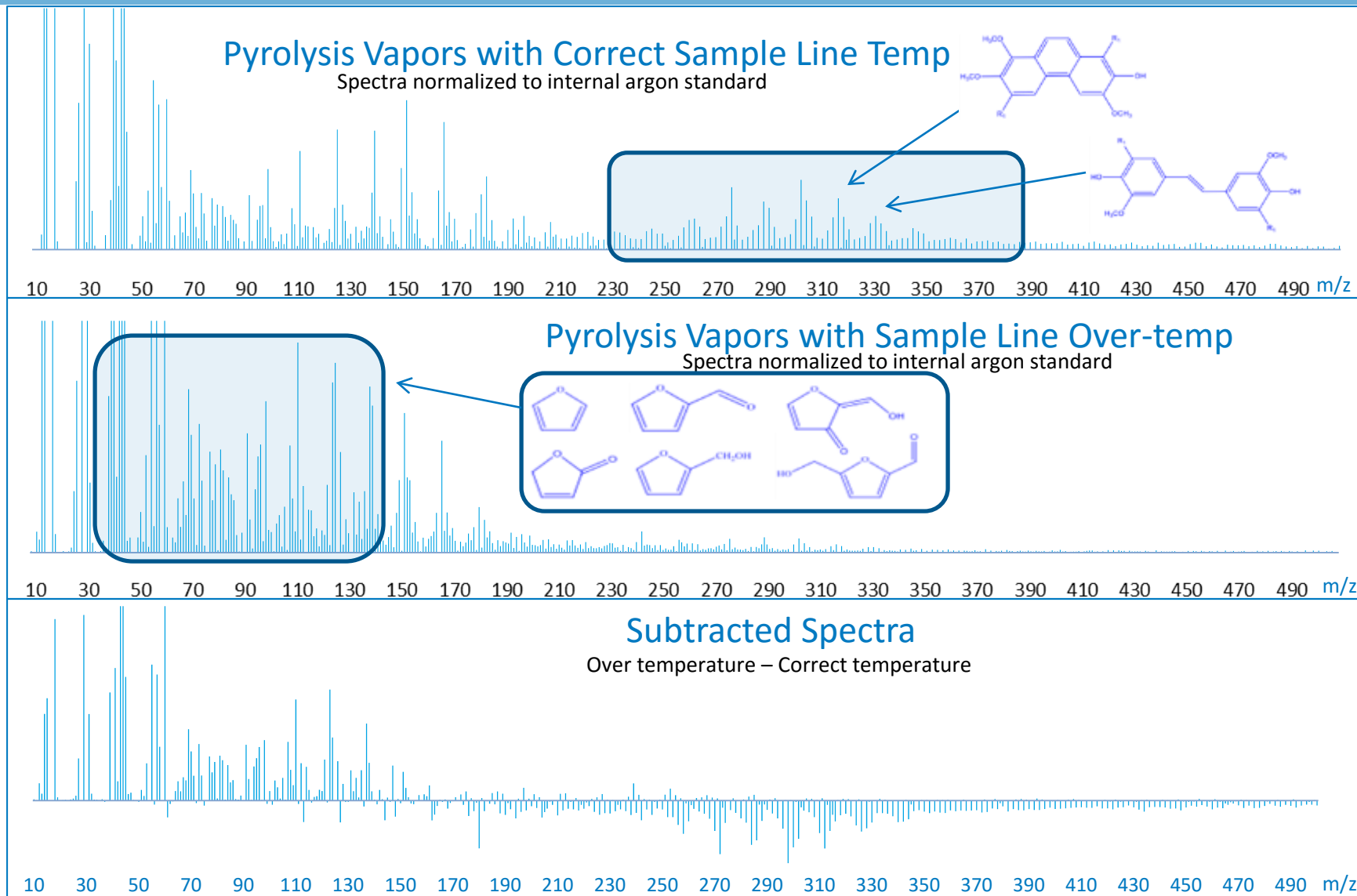


# Large Bench and Pilot Scale MBMS systems



- Transportable Systems
  - Continuous sampling
  - Multiple sample points
  - Typically 2 LPM flowby

# MBMS Spectra – Sample Line Over-temp



# Resonance Enhanced Multiphoton Ionization (REMPI)-TOF

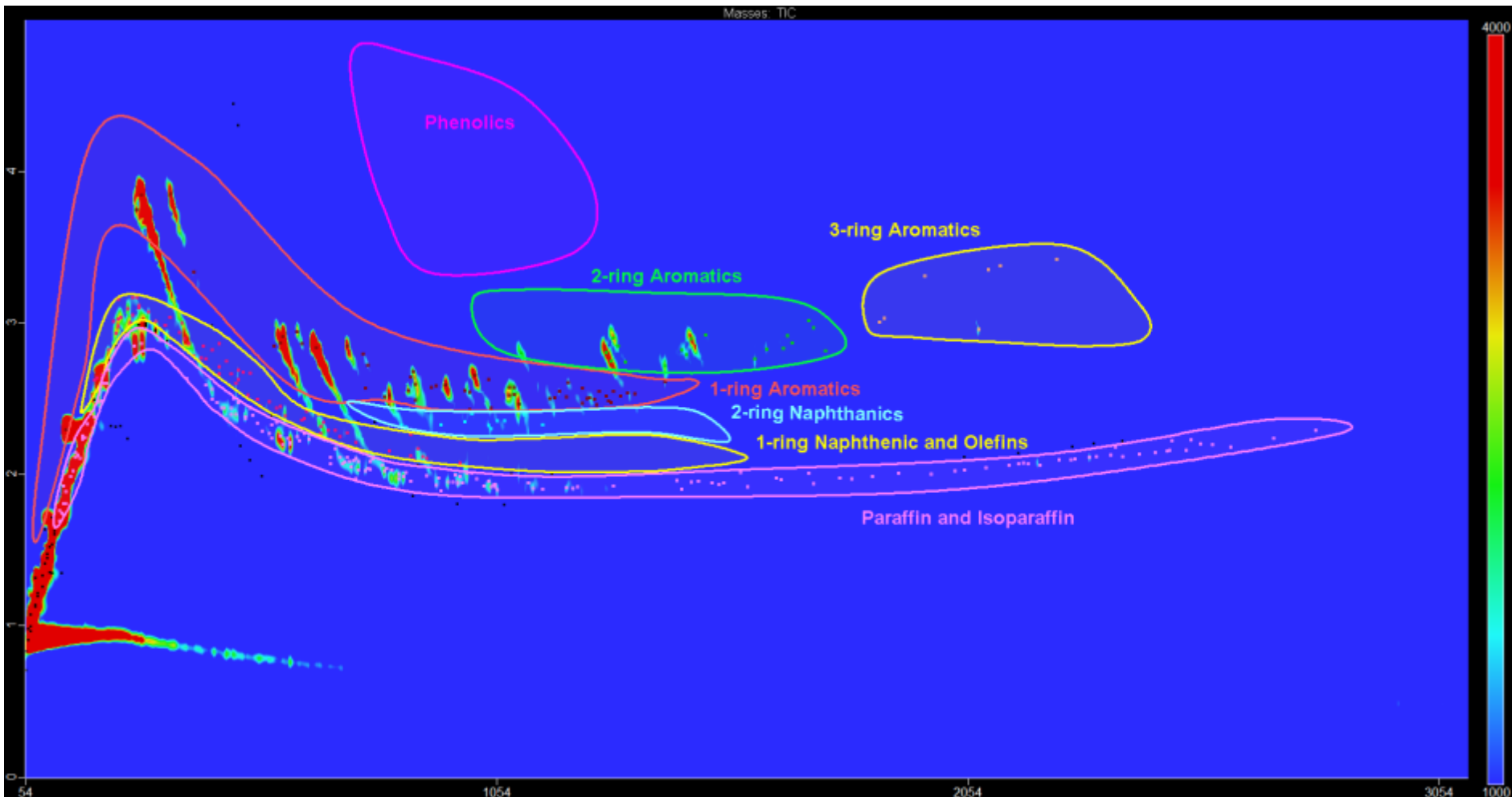
- MALDI and Tunable Laser Ablation with tunable REMPI UV ionization and He free jet expansion
  - 1600 (FWMH at  $m/z=78$ ) resolution
  - Selective ionization of lignin based aromatic hydrocarbons
  - Very clean spectra compared to other techniques
  - Could be adapted for online streams





- Post Analysis of Oils and upgraded Oil products
  - 1 AMU resolution
  - Strength is qualitative comparisons

# Best for comparisons of upgraded products



# Q-TOF Micro

- Q-TOF Micro
  - 5000 (FWMH) resolution
  - Electrospray, APCI, MALDI
  - Py-Oil analysis, Algal Proteins



# Single Magnetic Sector



- Single Magnetic Sector
  - 5000 resolution
  - EI and CI ionization
  - Capillary – Continuous
  - Direct Insertion Probe
- Measuring evolved gas composition of distillation curves in real time coupled with TGA

# FTMS – Currently being installed





# FTMS – Currently being installed

- 7 Tesla Magnet
  - >1 million resolution
  - ETD
  - APCI
  - APPI
  - MALDI
- Initial analysis
  - Algae Oils
- Future analysis
  - Condensable Tars or Pyrolysis oils and upgraded products

# NREL Strengths

- Capabilities to sample from many scales and reactor designs
- Sampling at high temperatures up to 500 C
- Knowledge of processes and integrations to utilize instrumentation for experimental design
- High throughput pipelines for biomass screening and catalyst development
- Experienced staff usually with 10+ years at NREL

# NREL Challenges

- Lack of personnel to analyze data
- Lack of funding to operate all instrumentation
- Aging instrumentation
- Lack of relevant high resolution libraries
- Determinations of unknowns
- Challenges in quantification of components

**NREL**  
NATIONAL RENEWABLE ENERGY LABORATORY

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Bioenergy

RESEARCH -- STAFF IMPACTS DATA & TOOLS -- FACILITIES -- WORK WITH US

"Valorization of these (lignin) waste streams could eventually play a key role for the economic viability and environmental sustainability of biorefineries."  
—Senior Engineer Gregg Beckham

[Read more about lignin valorization](#)



**PARTNERSHIPS**  
DuPont-NREL Partnership Delivered Key Innovations for Large Scale Cellulosic Ethanol Facility in Iowa



**INNOVATION**  
National Bioenergy Center accelerates the pace to move biofuels into the marketplace

**LABORATORY ANALYTICAL PROCEDURES**

- ▶ Biomass compositional analysis
- ▶ Bio-oil analysis
- ▶ Microalgal biofuels analysis

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May 24, 2016

**NREL Research Helps Convert Overabundant Methane into Useful Products**  
March 18, 2016

NREL's Bioenergy research supports the U.S. Department of Energy [Bioenergy Technologies Office](#) and the [Office of Science](#).

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# Acknowledgements



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[www.nrel.gov](http://www.nrel.gov)

