NREL
NATIONAL RENEWABLE ENERGY LABORATORY





Method for Hot Real-Time Sampling of Pyrolysis Vapors

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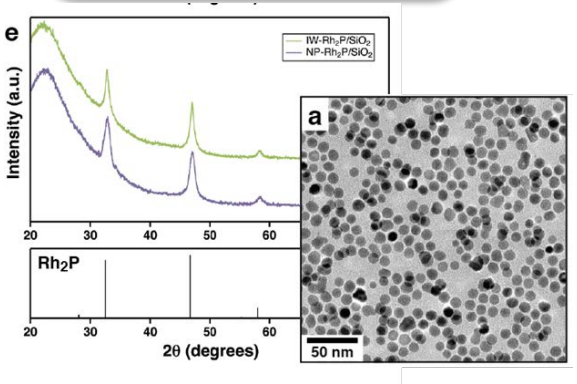
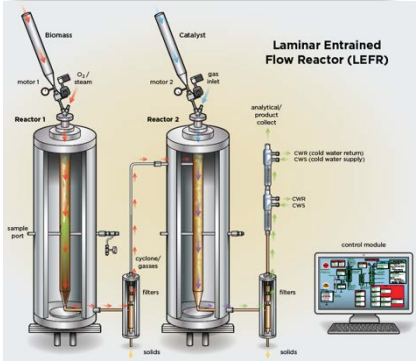
NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Finding Solutions for Biomass Conversion at NREL

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

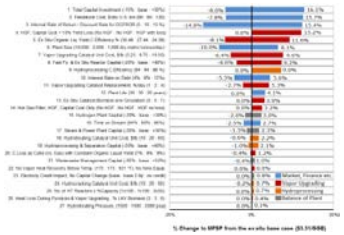
Fundamental Science mg-g → Catalyst Development & Testing g-kg → Scale-up & Demonstration 100's kg





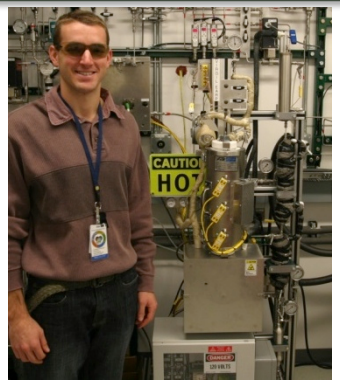
Overarching research necessary to support lab and industrial deployment.

Feedstocks | Bio-Oil Characterization | Gasification Products | Technoeconomic Analysis

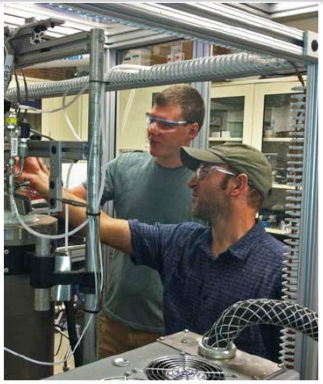


Thermochemical platform at NREL has multiple systems from mg to 450kg/day scales and operating in a variety of configurations

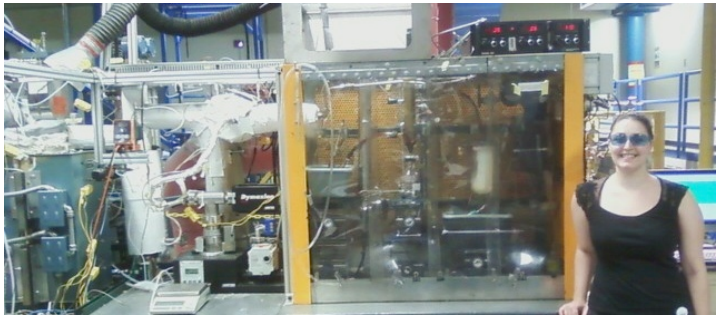
Small Scale Reactors:
Catalyst Development
Catalyst use per test: 0-2g



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

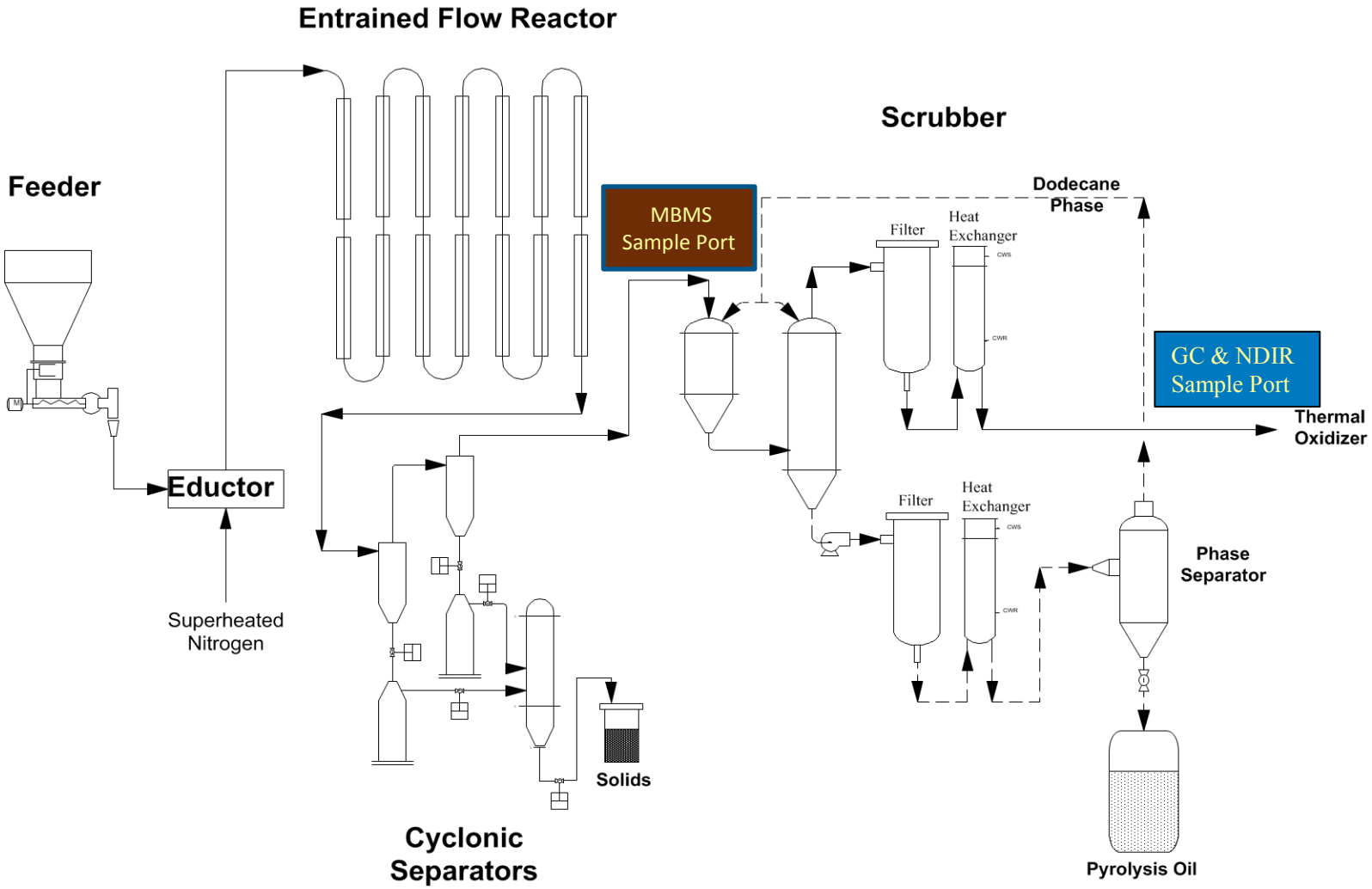


4” Fluidized Bed Reactor:
Gasification
Biomass rate: <2 kg/hr

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

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

TCPDU Process Flow Diagram for Pyrolysis



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

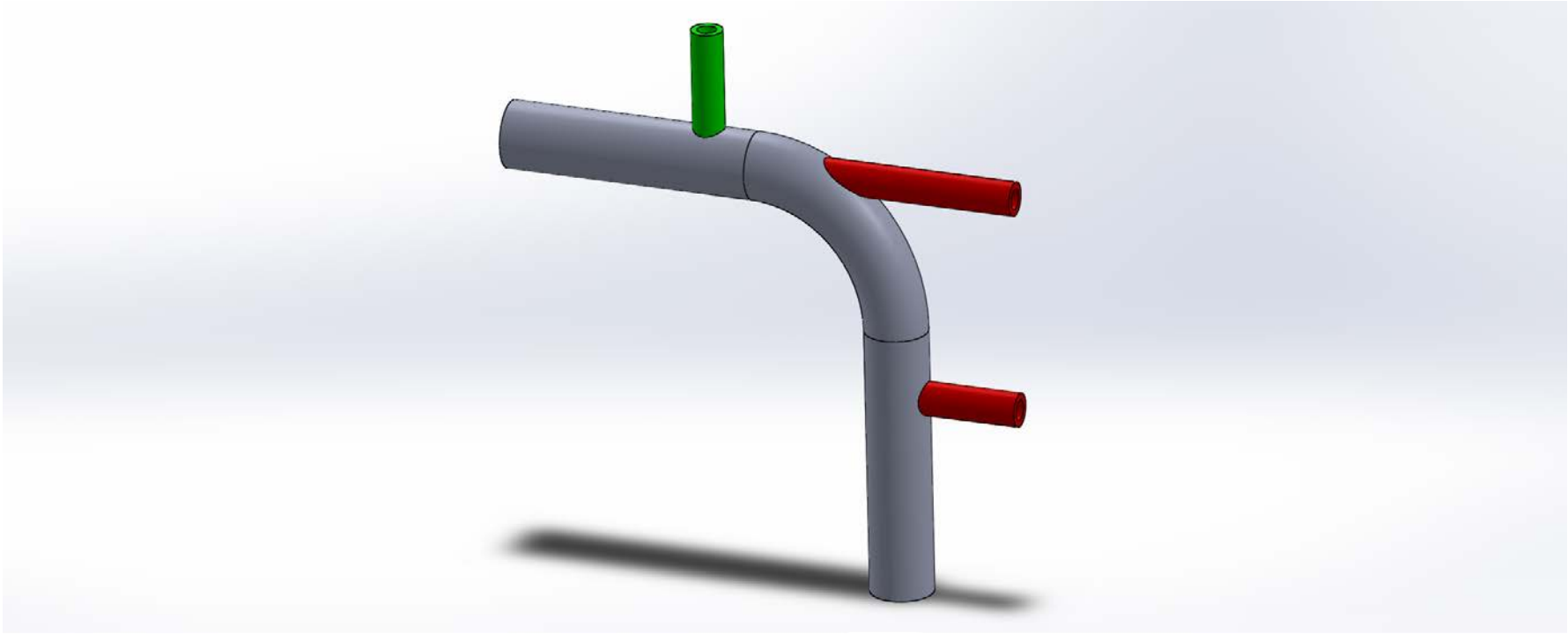
Challenges of Sampling at the Pilot Scale

- Operational Constraints
- Analytical equipment adversely affected by high ambient temperatures/dust
- Space around reactors required for plant maintenance and operation
- Multiple sampling points
  - Pre- and Post-catalytic Reactors
- Plugging and flow issues

- Representative Sample
- Residence time
  - Thermal changes
    - Cracking, further reaction chemistries
- Catalytic effects
  - Ash, char, anti-seize
- Even heating of lines
  - Prevent cracking, or full/ partial condensation of products

Guide to Successful Sampling – Sample Ports

- Position orthogonal prior to bends
  - Avoid in-line placement
- Place on upper half of pipe to prevent accumulated condensates from entering sample lines



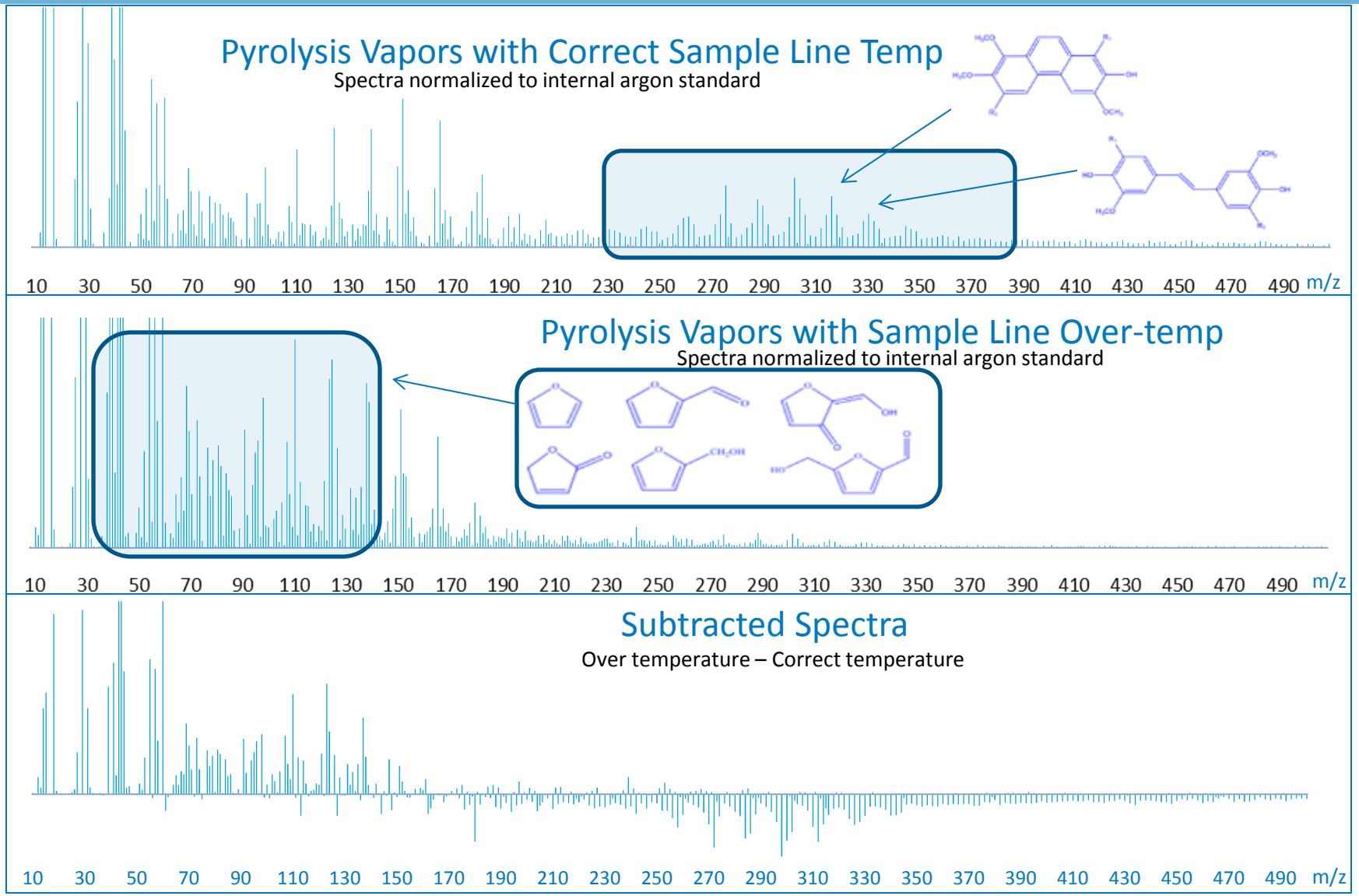
Guide to Successful Sampling - Filtration

- Filter as close to process as possible
  - Filter volume large enough to prevent particulate plugging
  - Sample volume small enough to prevent dilution or long residence times
    - Cracking of samples or catalytic changes due to particulate interaction
  - Appropriate filtration size for sampling equipment and tubing
    - TCPDU uses 10-15 µm elements

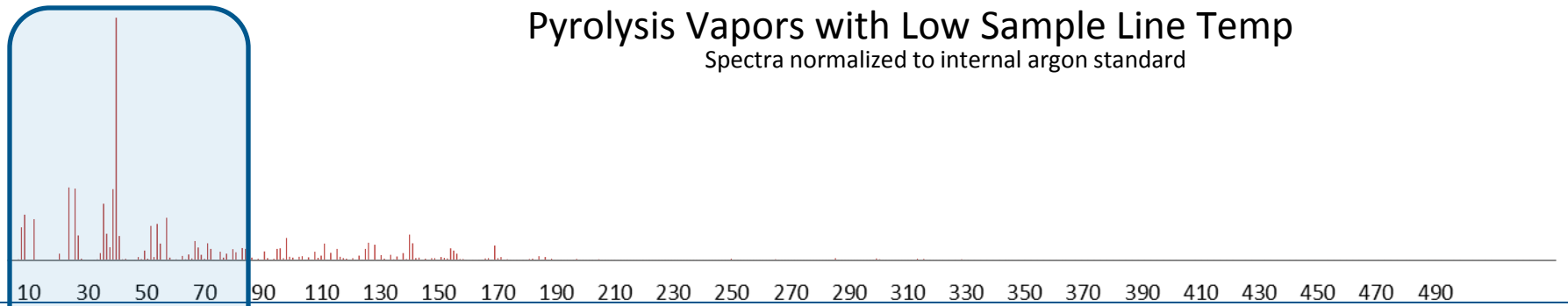
Guide to Successful Sampling – Even Heating

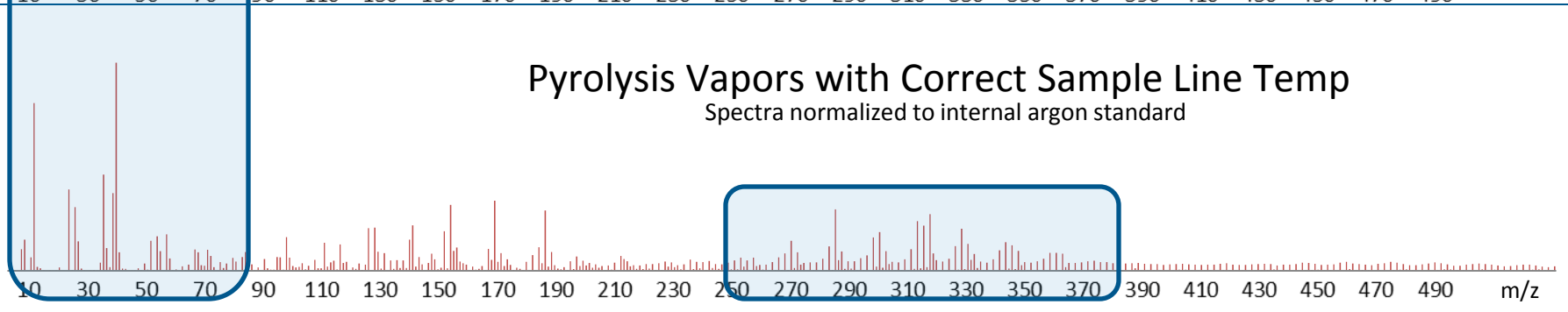
- Sample line temperatures must not change composition of vapor stream
  - Even a few degrees matter:
    - Too Hot can thermally crack the sample
    - Too Cool can partially or fully condensate a sample and promote plugging
  - Be careful of heat sinks like fittings

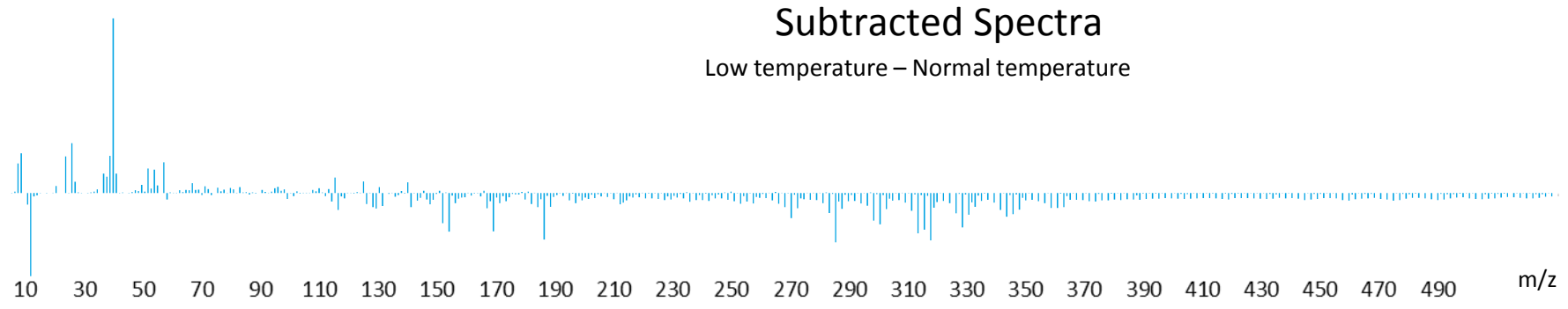
MBMS Spectra – Sample Line Over-temp



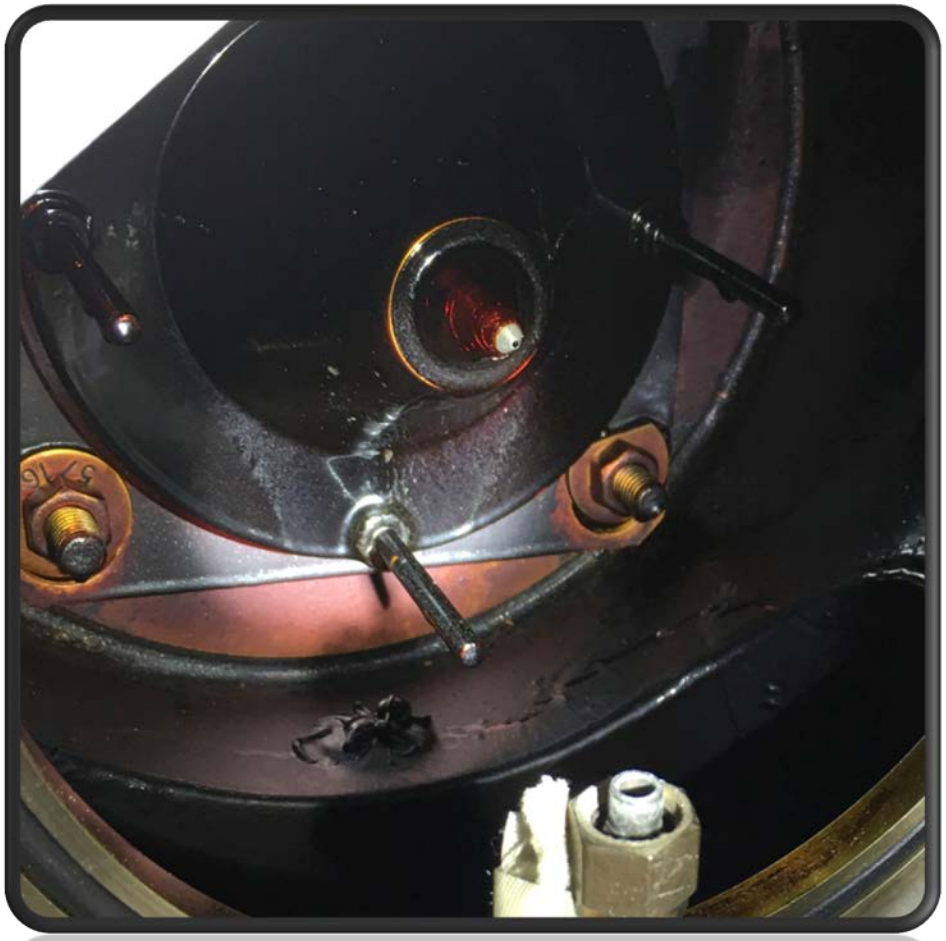
MBMS – Sample Line Low Temperature







Pyrolysis vapors are hard on analytical equipment



- Robust pumping systems required
- Frequent burnouts help
  - Watch for ash buildup
- Heated nitrogen purge when not actively sampling
- Redundant sample lines
- Material compatibility
  - Valve packing materials my pyrolize as well at temperature

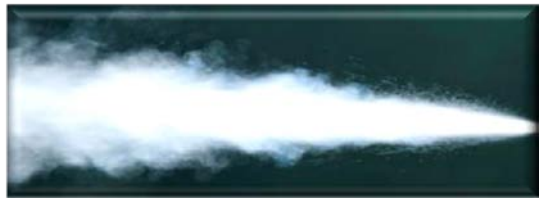
Aerosols

- Aerosols carry much further downstream than expected
  - Tend to drop out after pressure drops
    - Control valves
    - 90 degree bends
    - Pumps

Pyrolysis buildup in pump head – located after a condenser and coalescing filter

How to Deal with Aerosols

- Filter with coalescing filters if you have enough pressure
  - Work best when saturated
- Electrostatic precipitators



  - Creates RF interferences that can affect control system (requiring dedicated grounds) or interfere with analytical equipment such as Mass Spectrometers that use RF fields
- Knockouts after pressure drops
  - Longer sample latency for further analysis
    - Iced cotton-filled impingers for low pressure drop
- Tortured path
  - Requiring sample flow to change direction can help but may be a challenge to clean

Robust Sampling System - Summary

- Leave time for commissioning of sampling system
  - May need to optimize for an individual feedstock
- Place your sample ports effectively
- Filter close to the process
- Even heating of sample components is critical
- Effectively deal with aerosols
- Frequent cleaning required
- Analytical equipment must be designed for high temperatures and condensable components
- Adequate sample flow for as short a sample time as reasonable
- Utilize inert internal standards to compensate for flow issues

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Bioenergy Technologies Office

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