

# Method for hot real-time analysis of pyrolysis vapors at pilot scale

Marc Pomeroy  
National Renewable Energy Lab

## Abstract

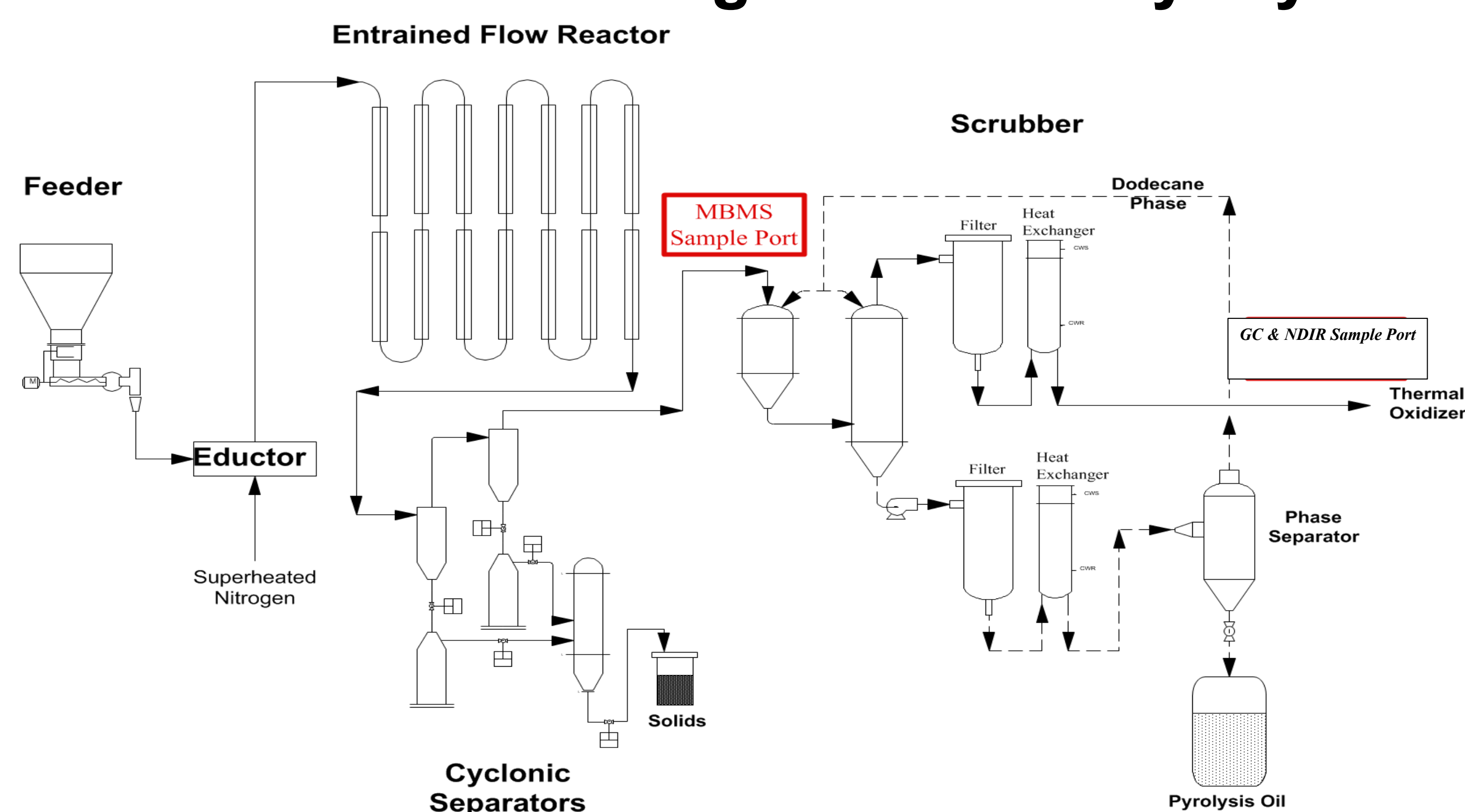
Pyrolysis oils contain more than 400 compounds, up to 60% of which do not re-volatilize for subsequent chemical analysis. Vapor chemical composition is also complicated as additional condensation reactions occur during quenching and collection of the product. Due to the complexity of the pyrolysis oil, and a desire to catalytically upgrade the vapor composition before condensation, online real-time analytical techniques such as Molecular Beam Mass Spectrometry (MBMS) are of great use. However, in order to properly sample hot pyrolysis vapors at the pilot scale, many challenges must be overcome.

NREL has a wide variety of reactor systems that are capable of studying biomass pyrolysis and gasification from the scale of mg of biomass to the 450kg/day pilot scale on the Thermochemical Process Development Unit (TCPDU). All scales are capable of hot real time sampling and MBMS comparisons. Sampling at the lab scale may only require a sample line of a couple centimeters in length with one heated zone, where sampling at the pilot scale may require the analytical equipment to be located multiple meters away utilizing many heated zones. This can cause many more challenges in obtaining a representative analytical sample at the analytical instrumentation as well as much larger operational and maintenance challenges due to plugging.



MBMS Molecular Beam Mass Spectrometer

## TCPDU Process Flow Diagram – Fast Pyrolysis



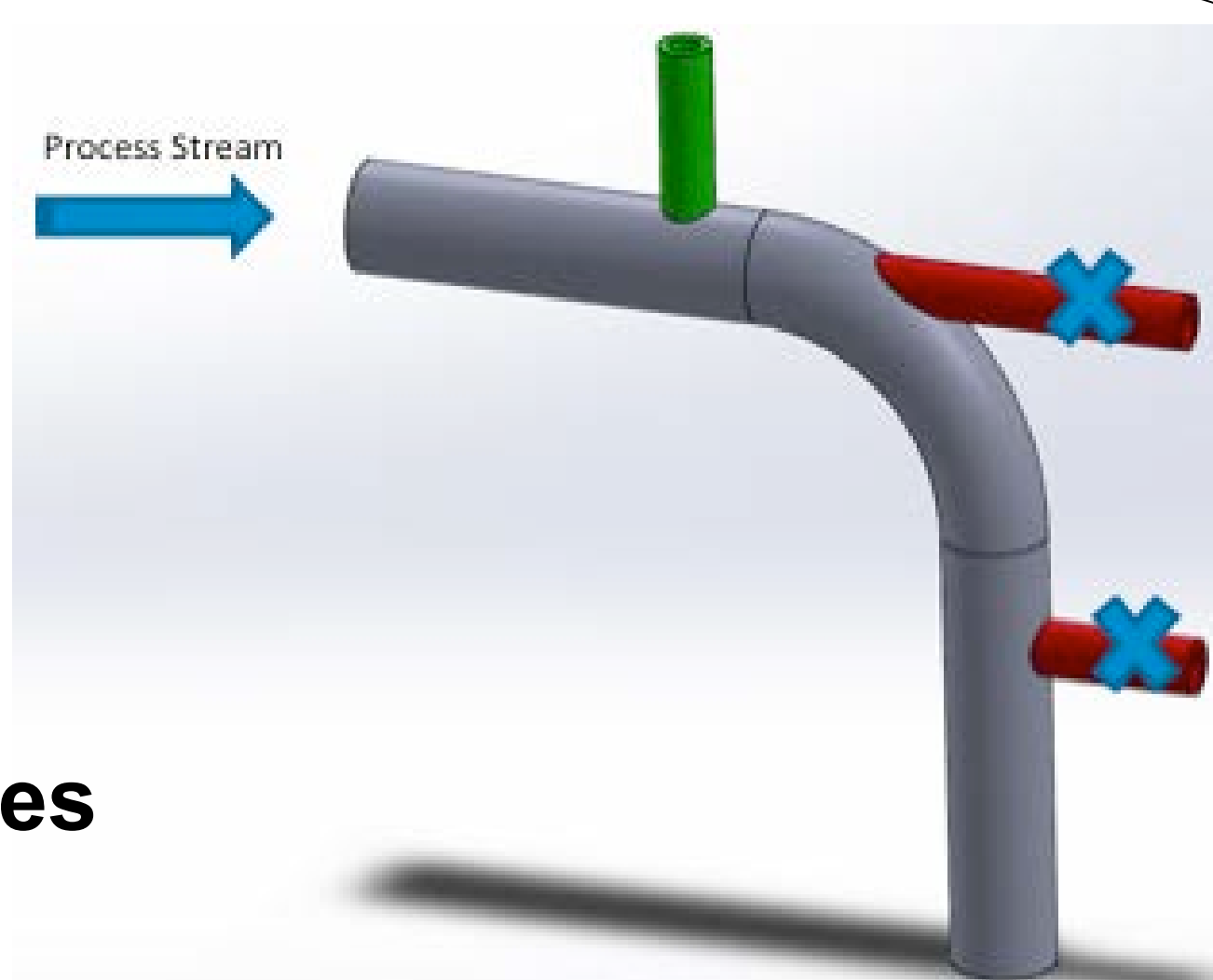
Success for sample integrity and operational robustness happens in the details:

### Minimize Residence Time

Vapor phase chemistry continues to change with time at temperature – Minimize sample line length, volume, and residence time to maintain sample integrity.

### Sample Line Placement

- Avoid inline sampling to minimize particulate matter carryover further downstream
- If sampling right at dew point, condensation can occur just after sharp bends
- Sample from the top side of pipe or vertical section to avoid any potential condensate issues



### Sample Filtering

- Filter as close to process to minimize particulate plugging of lines and valves
- Size housings to have minimal residence time to minimize thermal cracking and catalytic interactions with ash trapped on filter
- TCPDU filters to 10-15  $\mu\text{m}$  which is suitable for MBMS needs without immediately plugging

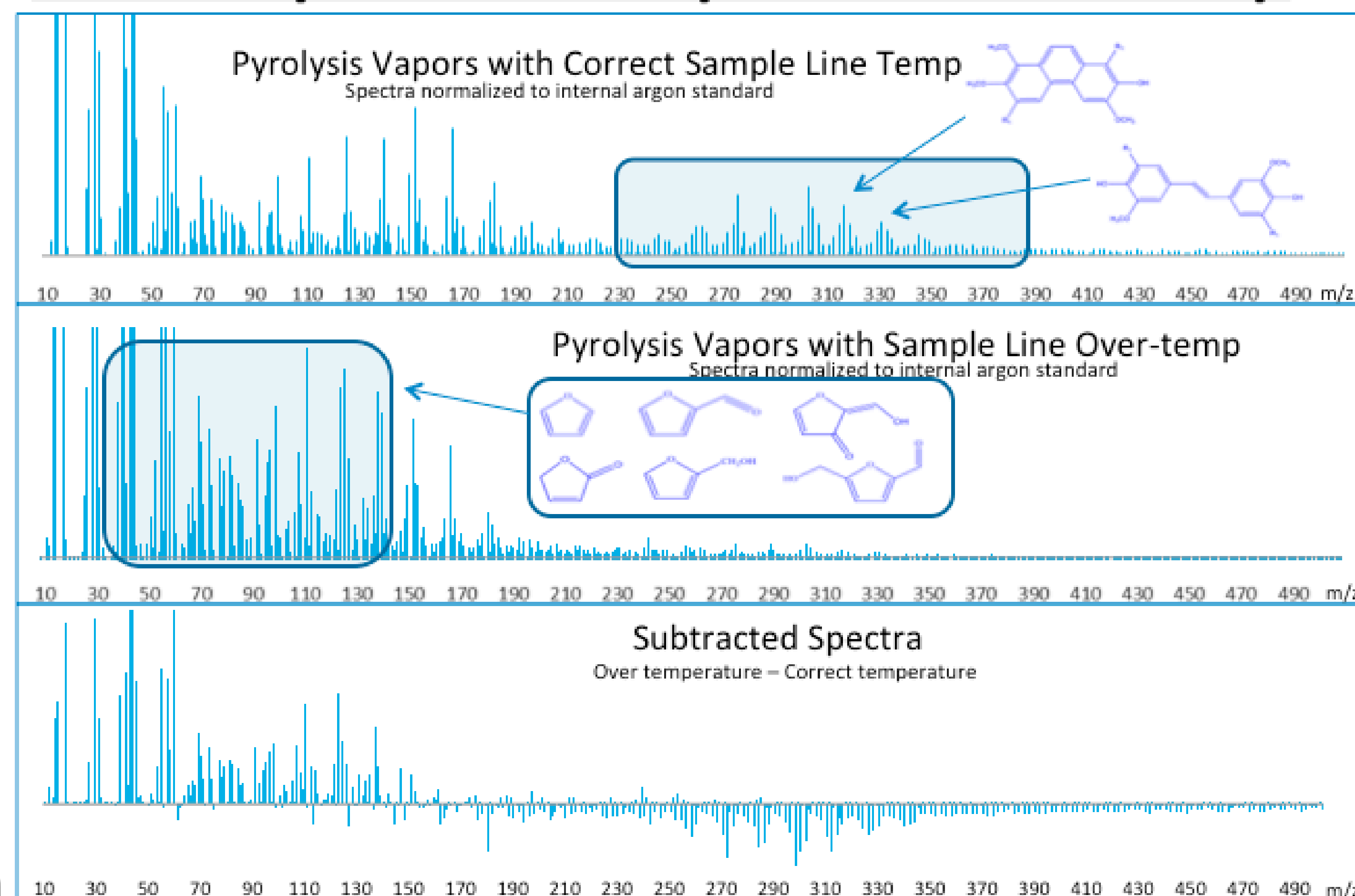


15  $\mu\text{m}$  stainless steel filters

### Consistent proper temperature control is critical

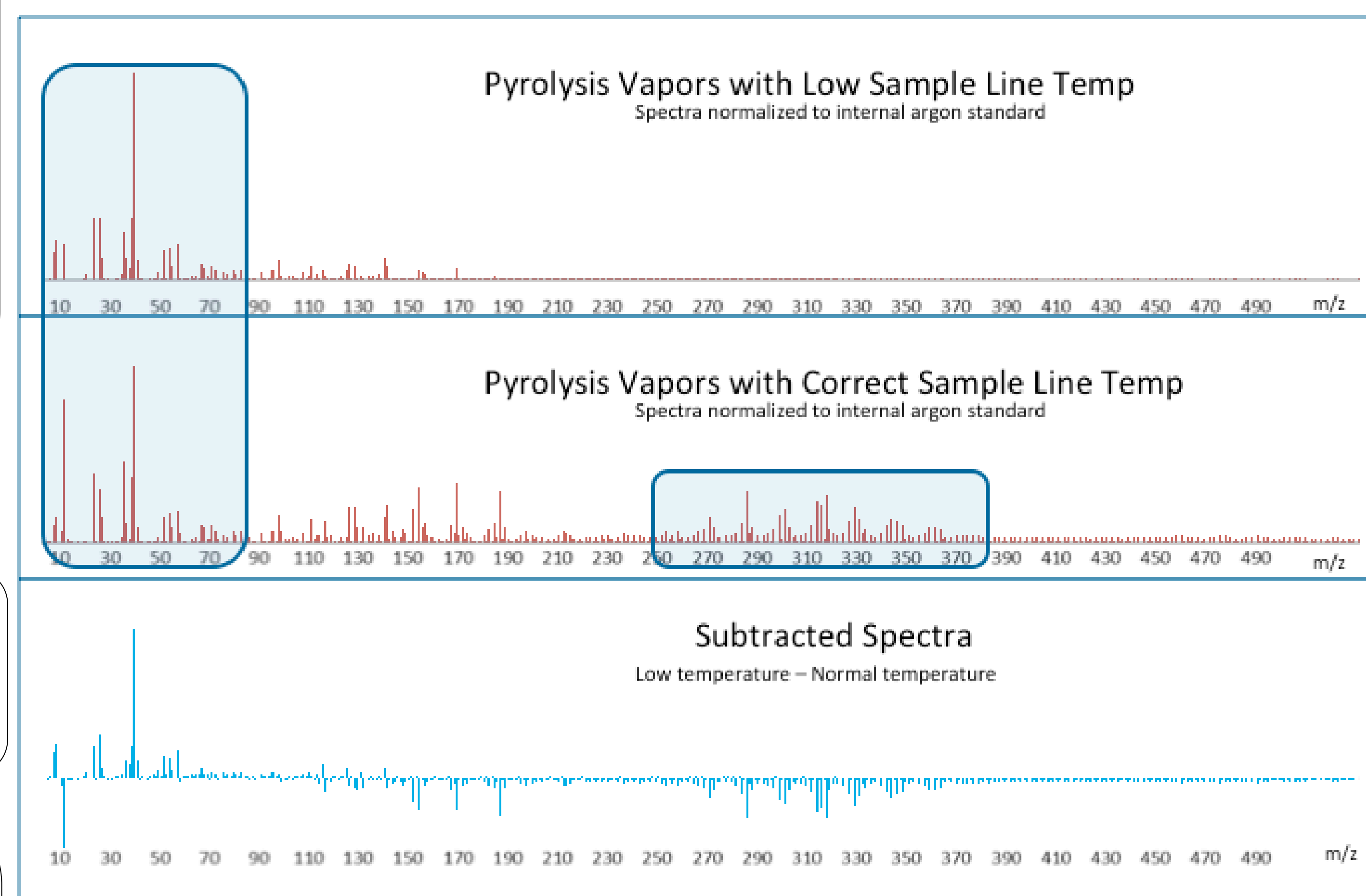
Low temperatures, even across small areas, can lead to partial condensation of products and operational issues due to plugging. High temperatures can cause thermal cracking and incorrect analysis of vapor phase products. This temperature range can be as little as 20° C and can be caused by heat sinks such as improperly heated fittings or too much heat applied over only a few inches.

## MBMS Spectra – Sample Line Over-temp



Over-temperature leads to thermal cracking of vapors with lighter products produced

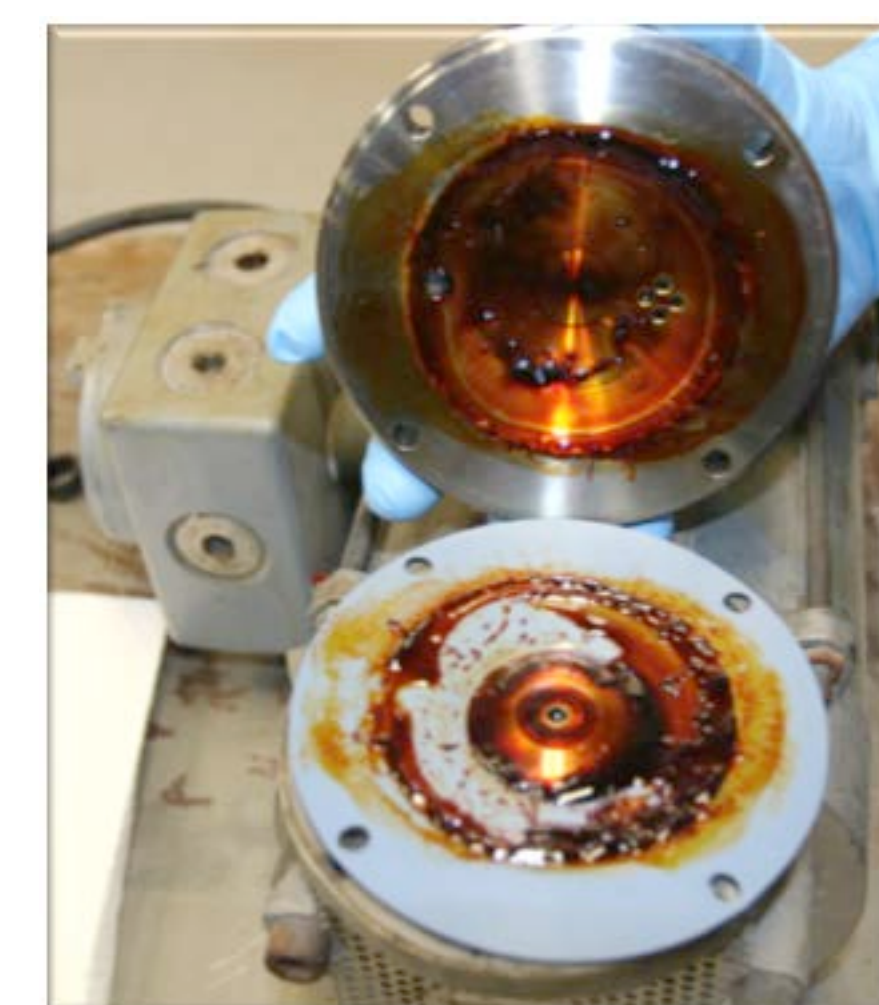
## MBMS – Sample Line Low Temperature



Low temperature leads to partial condensation of vapors with heavier components lost but no increase in lighter compounds

### Aerosols

Pyrolysis vapors are prone to aerosol formation and carry much further downstream than expected. These tend to drop out after pressure drops such as control valves or in high contact areas such as pump heads. Sufficient traps, filters, and condensers are required to minimize operational concerns.



Pyrolysis oil components from aerosols collected in pump head. Pump located after condenser and coalescing filter

Sampling biomass derived pyrolysis vapors is very difficult both operationally and experimentally. However, real time data of vapor phase components is extremely valuable for catalytic and process development.