# 2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

## Biomass Derived Pyrolysis Oils Corrosion Studies

**May 22, 2013**
**Bio-Oil Technology Area Review**

**James R Keiser**
**Oak Ridge National Laboratory**

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

# Goals/Objectives

**The presence of significant concentrations of oxygen-bearing compounds, including water and carboxylic acids, makes biomass derived oils very corrosive to some common structural materials**

## The goals of this project are:

**1) Use conventional and developmental techniques to fully characterize bio-oil intermediates and products**

**2) Assess the corrosivity and compatibility of materials (alloys, elastomers, plastics, and sealants) with as-produced and treated bio-oils**

**3) Identify or develop materials specifically suited for pyrolysis oil environments**

# Project Quad Chart Overview

## Timeline

- Project started – Oct, 2010
- Duration – FY2016

## Barriers

- Tt-E Pyrolysis of Biomass

## Budget

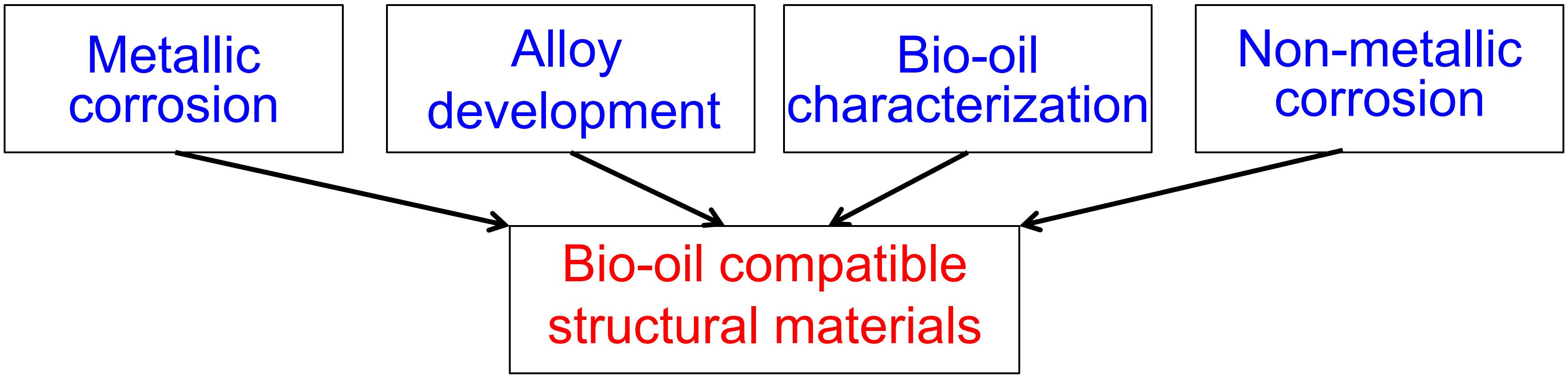
- Total project funding - $1,370K*
- Funding received in FY 2011 - $160K*
- Funding in FY 2012 - $160K*
- Funding for FY 2013 - $1,050K
- ARRA Funding - none
- Project funded for 3 years with average annual funding of $456.7K

*not including $40K/year to Sokhansanj in FY11 and FY12

## Partners & Roles

- PNNL – provide test fluids, exposure sites & project guidance
- NREL – provide test fluids & exposure sites
- Iowa State – provide test fluids & exposure site
- BNL – collaborate on non-metallic studies
- Other contributors of bio-oil

# Project Overview




- Characterize bio-oils to identify critical components
- Characterize the degradation of metallic and non-metallic materials by biomass derived bio-oil
- Determine the mechanism(s) responsible for degradation of potential structural materials used in biomass pyrolysis systems
- Identify and/or develop materials compatible with bio-oil <u>production</u>, <u>processing</u>, <u>storage</u> and <u>transport</u> to assist successful commercialization of bio-oil production technologies

# Approach

- Analysis techniques of bio-oils and corrosion products will be essential in determination of degradation mechanism(s)
  - Existing and new techniques as needed

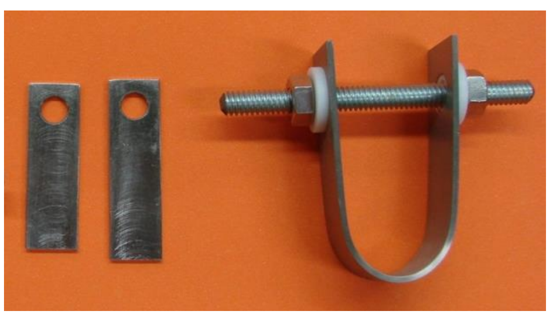
- Characterization of actual component degradation from operating systems, field exposures of test materials, laboratory corrosion simulations of test materials
  - Employ advanced electron microscopy and chemical analysis techniques

- Identify or develop alternate materials with sufficient resistance to degradation. Analysis will focus on lowest cost alloys that meet goals

- Technical success based on
  - Assessment and determination of degradation mechanism(s)
  - Successful identification of sufficiently low cost degradation resistant materials to aide advancement of bio-oil technologies to the commercialization stage

# Technical Accomplishments/ Progress/Results – Metallic Corrosion

- Laboratory corrosion studies involve exposing samples of selected alloys in and above bio-oil at selected temperatures
- Samples have been provided to operators for exposure in operating systems
- Components from operating systems have been examined by advanced characterization techniques
- Off-site, non-destructive measurements are being made



Typical corrosion samples

High pressure test system

Atmospheric pressure test systems

# Corrosion Rates Measured With As-Produced Bio-Oil And Treated Bio-Oil

- As-produced (raw) and stabilized bio-oil give unacceptably high corrosion rates at 50°C for carbon steel and 2¼Cr-1Mo steel
- Some bio-oils cause significant corrosion of even 410 stainless steel (12% Cr) at 50°C
- Cracking observed in some stressed samples
- **Reduction of oxygen content to 3.3% was sufficient to make the bio-oil non-corrosive to carbon steel even at elevated temperature**

# For Samples Immersed In 50°C Pyrolysis Oil, Corrosion Rates (mm/yr) Were Calculated From Weight Changes

| | C1018 carbon steel | | 2¼ Cr-1 Mo | | 409 stainless steel | | 304L stainless steel | | 316L stainless steel | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Coupon | U-bend | Coupon | U-Bend | Coupon | U-bend | Coupon | U-bend | Coupon | U-bend |
| NREL pyrolysis oil Liquid | 0.9 | 2.4 | 0.2 | 0.2 | 0.1 | ----- | 0.0 | ----- | 0.0 | 0.0 |
| | | | | | | | | | | |
| Univ of Mass pyrolysis oil-Liquid | 2.6 | 2.4 | 3.3 | 3.3 | 0.6 | 0.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | | |
| VTT pyrolysis oil Liquid | 2.8 | 3.1 | 4.0 | 4.2 | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | | |
| Unidentified pyrolysis oil-Liquid | 2.6 | 0.2 | 2.4 | 2.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | | |
| USDA-ARS pyrolysis oil Liquid | 0.6 | 0.6 | 1.4 | 1.5 | 0.8 | 0.8 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | | |
| PNNL stabilized oil-Liquid | 2.1 | 2.2 | 3.0 | 3.2 | 0.8 | 1.1 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | | |
| PNNL hydrotreated oil – 3.3% oxygen | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | | |
| PNNL hydrotreated oil – 1.3% oxygen | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

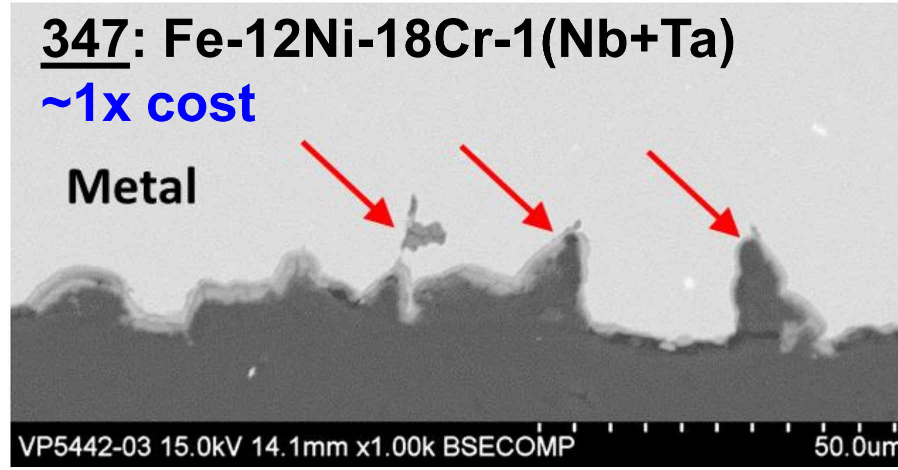
The results highlighted in red are for conditions where the calculated corrosion rate projects to more than 0.25 mm/yr (0.010 inches/year)

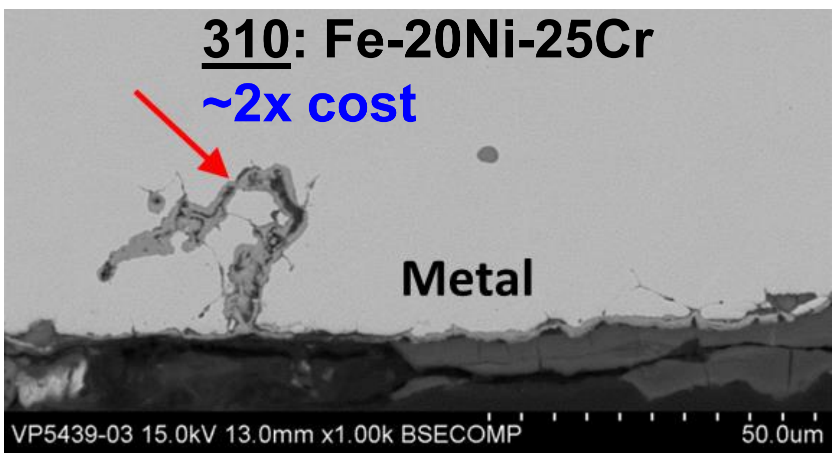
# Technical Accomplishments – Assessment Of Alloys For Process System Components

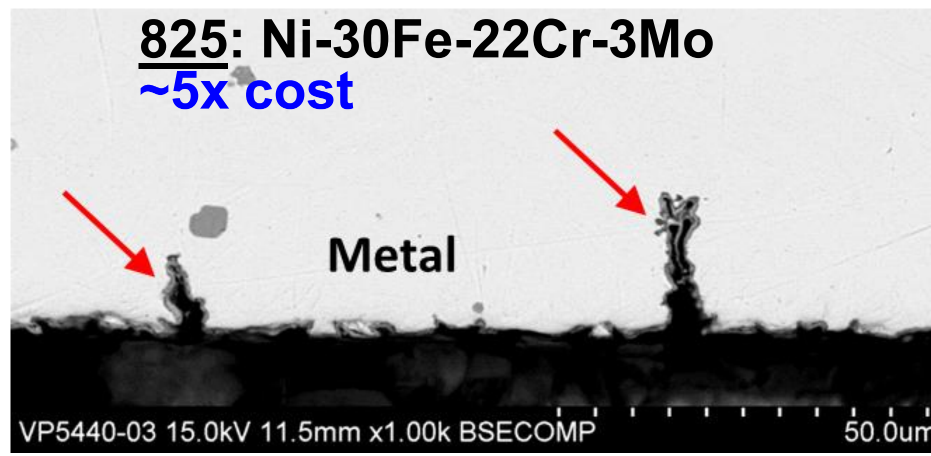
- During this first year, the primary effort has been to examine materials exposed to the environments associated with production and processing of bio-oil
- Examinations have included:
  - 1) pipe sections/corrosion coupons of candidate materials specifically fabricated for exposure in operating systems,
  - 2) components removed from operating systems for characterization and assessment of durability
  - Characterization techniques have included dye penetrant inspection, light microscopy and scanning electron microscopy of cross sections as well as elemental analysis techniques such as EDS and electron microprobe

# NREL Pyrolysis/Gasification Transfer Pipe Sections Show Attack Of Internal Surfaces

- **Cross sections of transfer line segments of different alloys**

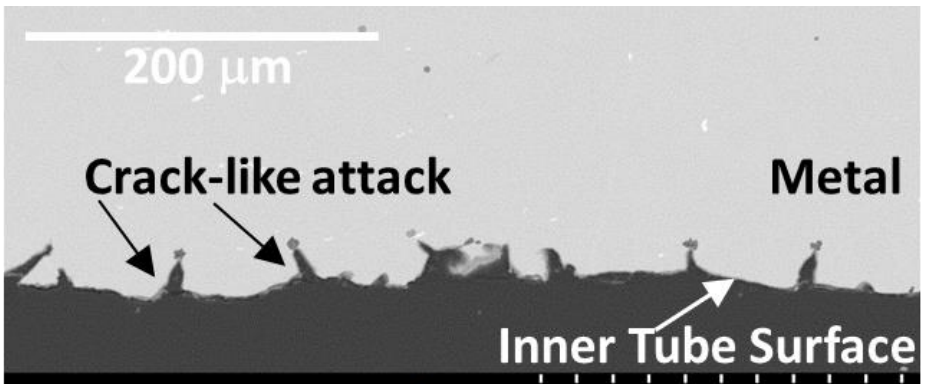




550°C alloy corrosion during pyrolysis oil production may be a key issue

**316, 347, 310, 800, and 825 alloy segments all showed corrosion/attack**

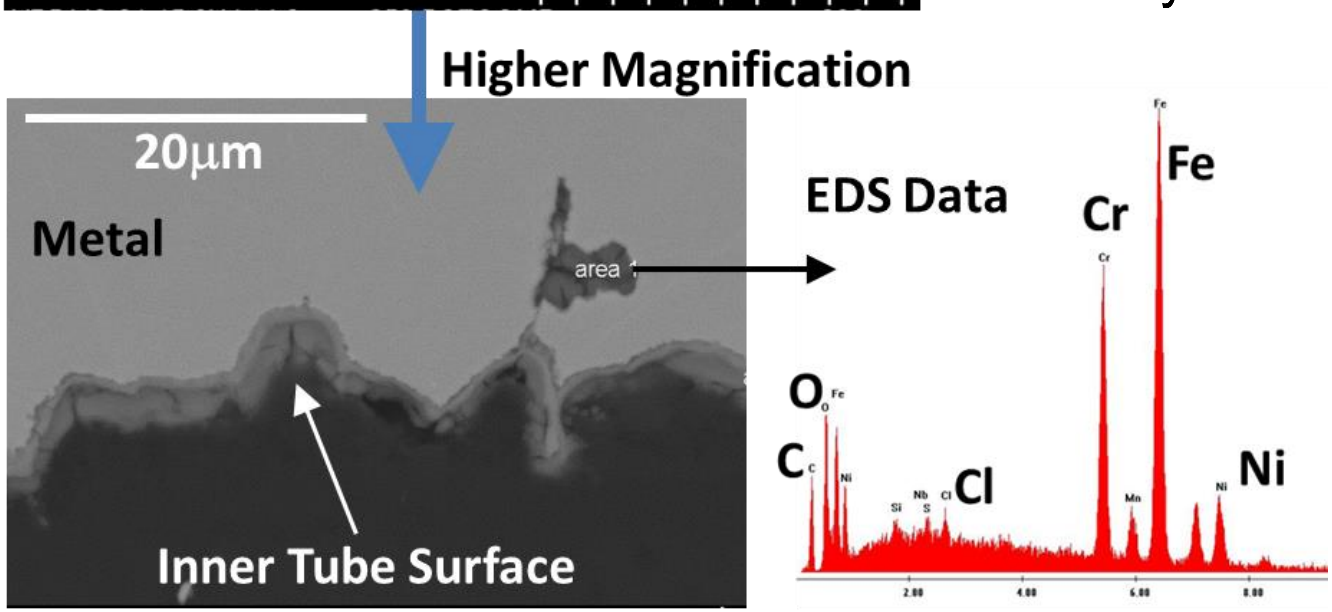
# Attack Of NREL Transfer Pipe Associated With Penetration Of C, Cl, And O

## •SEM/EDS Analysis of 347 Stainless Steel Segment




•Exposed to both fast pyrolysis and gasification (details not available)

•Suggests concerns for long-term durability



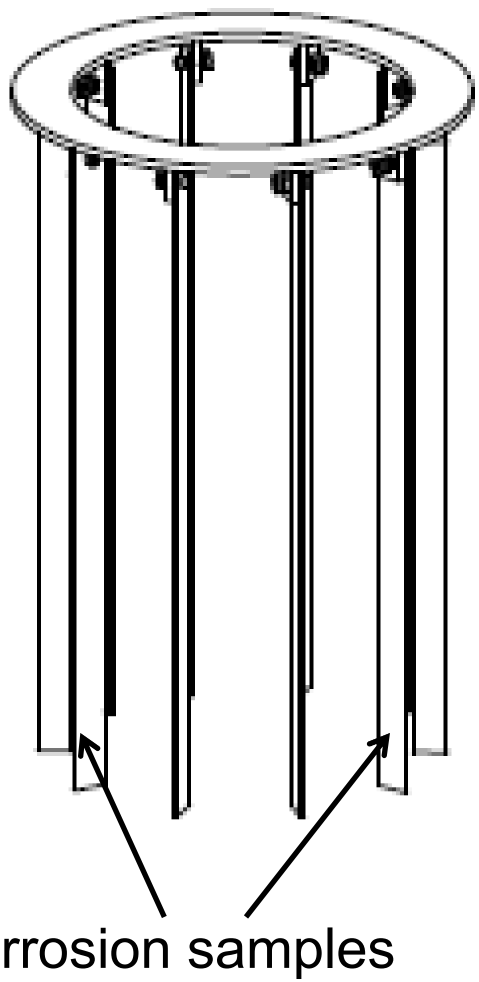
# Through A Collaboration With Iowa State University, Samples Of Selected Alloys Are Being Exposed In Their Pyrolysis Reactor

•5 alloys and duplicates under exposure at Iowa State fluidized bed pyrolysis reactor

•Alloys were selected to represent a range of low to high cost stainless steels

•Initial baseline exposure for 40 hours for corrosion assessment and mechanistic baseline

•Second set of samples will be exposed in longer duration testing to obtain kinetic trends and provide insight for lifetime modeling



# Approach To Analysis Techniques Development

Borrow from energy industry, develop new approaches to accommodating polarity & oxygenation

- ModTAN: ASTM D664 with intense extraction and hydrophilic titration solvent
- Acidified organic GC-MS/basified anion CE, CE-MS: chromatographies tailored to phase miscibility
- Aldehyde/ketone LC-MS: derivatization to enhance detection of oxygenates
- TDP-GC-MS: direct sampling of corrosive organic fractions and deposits thermal gradient & finally pyrolyzing environment

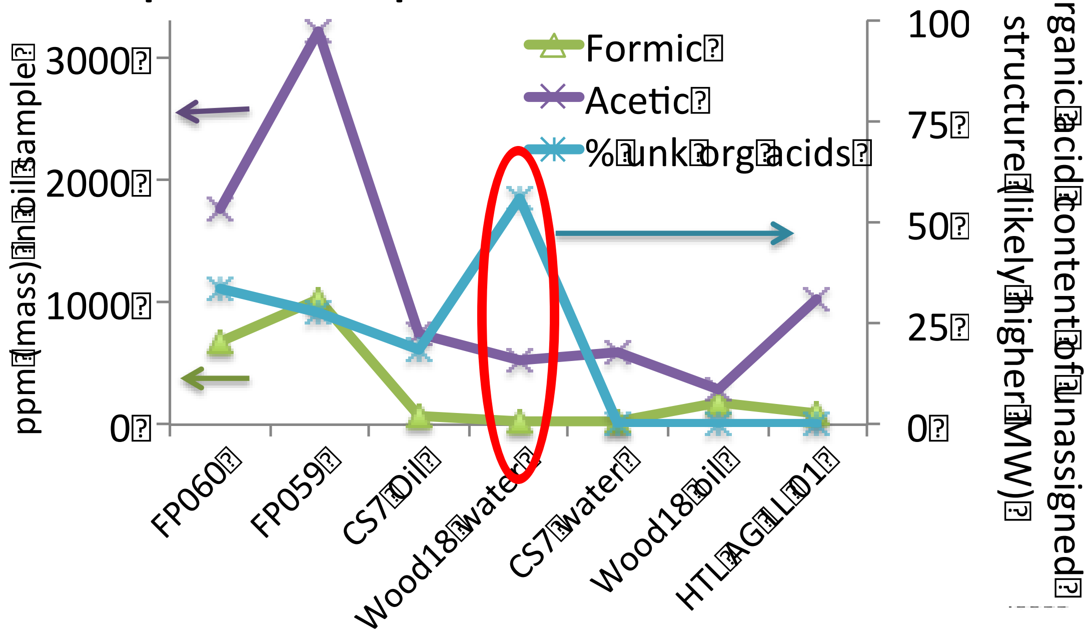
| ***ModTAN*** | ***CE*** | ***CE-MS*** | ***LC-MS*** | ***GC-MS*** | ***TDP-GC-MS*** |
|---|---|---|---|---|---|
| Acetic&formic acid | | ⇧ MW acids | Ald/Ket | Smaller HCs | larger HCs, chars |

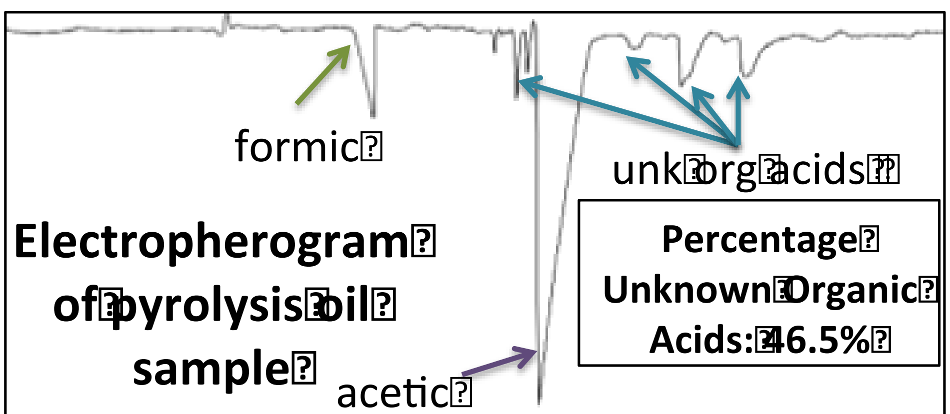
Decreasing polarity, oxygenation

# Current Work

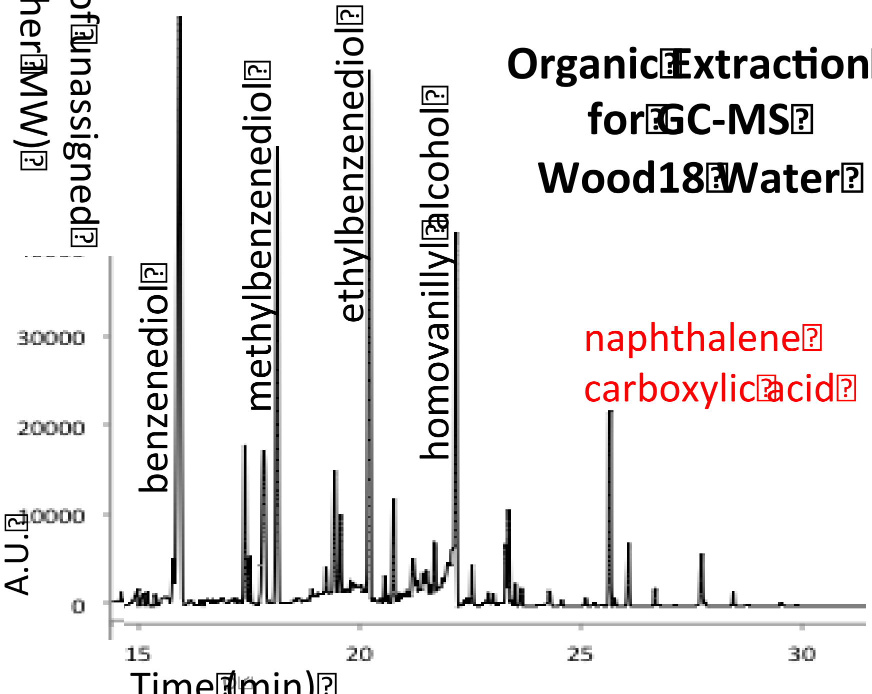
## *Investigating samples from universities, partner labs, international sources in concert with metal corrosion studies*

**Acid Speciation: Aqueous Extractions for CE**



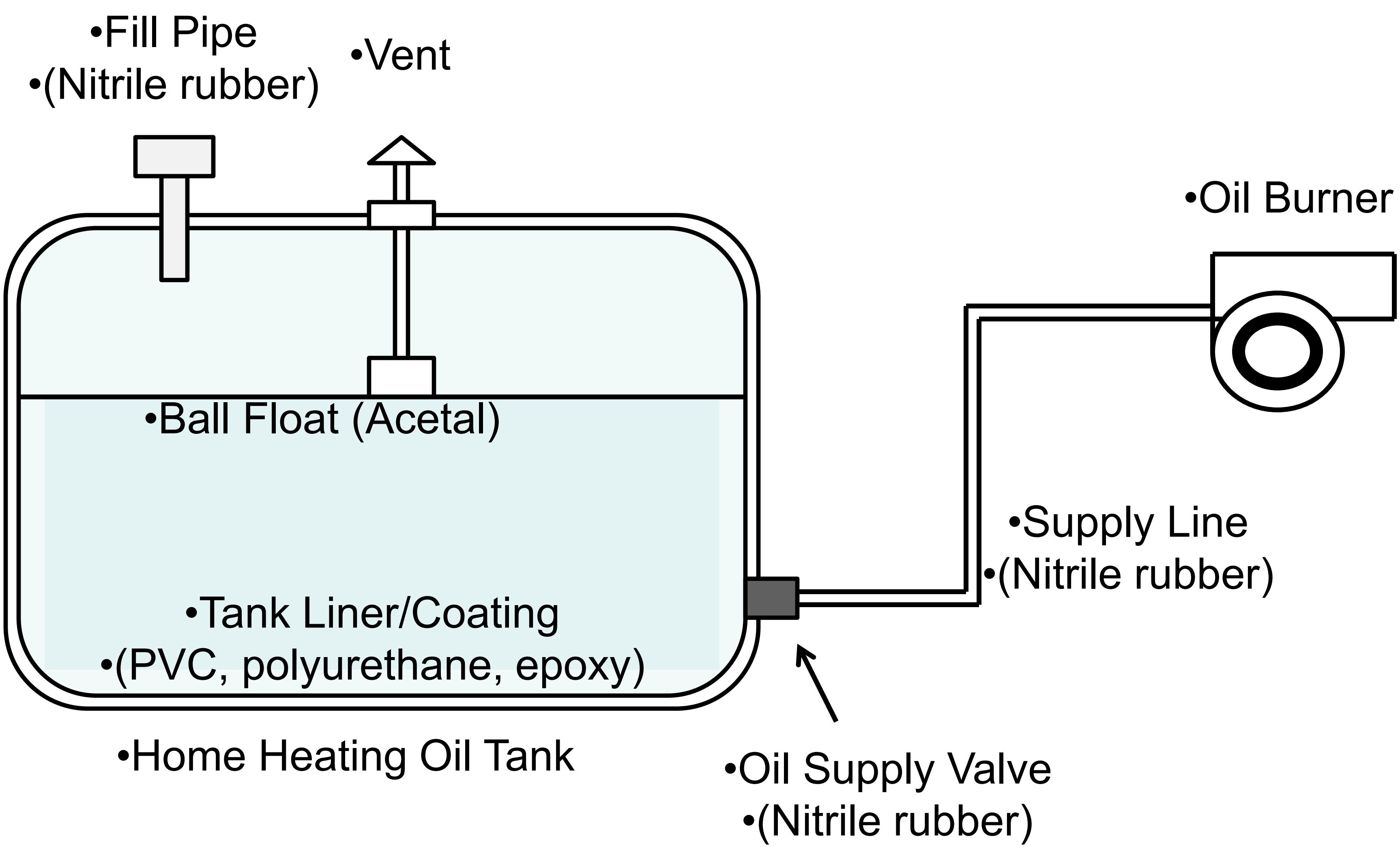

**Organic Extraction for GC-MS Wood18 Water**



# Polymer Compatibility Of Bio-Oil For Home Heating

- Objective:  to assess compatibility of home heating oil (containing 20% bio-derived oil) to fuel storage and delivery infrastructure polymers.
- This effort is a collaboration between ORNL, BNL, PNNL, and Stony Brook University.
- Test Methodology
  - Immerse specimens in representative test fuels for 4 weeks for elastomers and 16 weeks for plastics
  - Measure the change in mass, volume and hardness
  - Perform Dynamic Mechanical Analysis to determine the glass transition temperature.
- Status:
  - currently surveying potential sources for upgraded bio-oil
  - Currently reviewing literature and surveying industry manufacturers to properly identify and select relevant materials.

# Home Heating Oil System Diagram Showing There Are Many Polymer Materials Used In The Storage And Transport Of Home Heating Oil



# Relevance

- The technologies for producing the biomass-derived products require handling materials that can be quite corrosive because of the organic acid and water content
- To meet the platform's production and cost goals it is essential that the least expensive structural material with adequate corrosion resistance be identified
- This project is particularly relevant to the bioenergy industry because development of new analysis tools and identification or development of corrosion resistant alloys and non-metallic materials should prevent materials issues from stopping the success commercialization of the most promising bio-oil production technologies

# Critical Success Factors

- The first step will be to successfully characterize the biomass-derived oils and to determine their aggressiveness toward both metallic and non-metallic structural containment materials
- Bio-oils derived from different biomass sources will likely have some differences in composition and properties so a wide range of materials will need to be studied
- Successful identification of metallic and non-metallic materials with satisfactory resistance to bio-oils derived from a wide range of biomass types will be the ultimate measure of success for this project
- It is important to note it is likely there is not a “one shoe fits all” solution but materials will need to be selected on the basis of corrosion resistance, cost, fabricability, etc. for each process technology and biomass source

# Future Work

- During the next 16 months, efforts will continue to characterize bio-oils and to determine their effects on metallic and non-metallic materials
- Sets of bio-oil fractions produced from red oak and from corn stover are being produced by Iowa State, and these will be characterized for organic components and will be used in corrosion studies
- To the greatest extent possible, efforts will be made to produce or acquire samples or components with extended service times
- Results of corrosion tests and component examinations will be used to select material for further testing

# Summary

- Project Approach

- Characterize bio-oil and degradation of materials, identify alternate materials and new analysis techniques

- Technical Progress and Accomplishments

- Determined corrosion mechanism and corrosion resistant materials for some conditions

- Project Relevance

- Essential to identify materials that are compatible with bio-oils

- Critical Success Factors

- Identification of materials with sufficient corrosion resistance that materials will not prevent commercialization of technologies

- Future Work

- Expose samples in operating systems, examine system components, continue laboratory corrosion studies

- Technology Transfer and Collaborations

- Publish and present results at conferences and in project meetings

# Additional Slides

# Responses to Previous Reviewers' Comments

- The previous review was conducted a short time into the project, and reviewers generally provided very favorable comments
- The previous presentation included information on the torrefaction studies being conducted at UBC, and reviewers asked how the projects were connected – Answer – both are thermochemical processing methods, and torrefied wood could be used as feed for pyrolysis
- Another reviewer asked if there wasn't already enough information available on pyrolysis oil while another asked how we would deal with the constantly evolving processes and the resultant changes in bio-oil properties Answer – continued studies are needed to address the changes in bio-oil that are a result of process changes

# Responses to Previous Reviewers' Comments

- Other reviewers noted that we need to maintain an effort to stay aware of the progress being made in Europe
  Answer – We are participating in international conferences whenever possible and we make an effort to learn what is being done in Europe – however, we could probably do better at this
- A few reviewers commented on the lack of industrial involvement and the need for their participation
  Answer – industrial organizations are very protective of their proprietary information and are reluctant to participate. We will continue to make contacts and to be available when they need help addressing corrosion issues; this often gives an opportunity for further collaboration

# Publications and Presentations

- Publications and presentations for four conferences
- “Corrosivity of Pyrolysis Oils”, James R Keiser, Michael A Bestor, Samuel A Lewis, Sr., and John M Storey, presented and published in proceedings of 2011 TAPPI PEERS Conference, Portland, OR, October 2-5, 2011.
- “Corrosion Studies Of Raw And Treated Biomass-Derived Pyrolysis Oils”, James R Keiser Michael Howell, Samuel A Lewis, Sr, and Raynella M Connatser, Paper C2012-0001645, presented and published in proceedings of NACE International Corrosion 2012, Salt Lake City, UT, March 11-15, 2012.
- “Corrosivity And Composition Of Raw And Treated Pyrolysis Oils”, James R Keiser, Michael Howell, Raynella M Connatser, Samuel A Lewis, Sr., and Douglas C Elliott, Approved presented and published in proceedings of 2012 TAPPI PEERS Conference, Savannah, GA, October 15-17, 2012.
- “Degradation Of Structural Alloys In Biomass-Derived Pyrolysis Oil”, James R Keiser, Raynella M Connatser, Samuel A Lewis, Sr and Michael P Brady, to be presented at the 8$^{th}$ International Black Liquor Colloquium, Belo Horizonte, Brazil, May 19-23, 2013.

# Project Participants

- Project PI – James Keiser
- Task 1 leader – James Keiser
- Task 2 leader – Michael Brady
- Task 3 co-leaders – Samuel Lewis and Raynella Connatser
- Task 4 leader – Michael Kass