2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Materials Degradation In Biomass-Derived Oils

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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Goals/Objectives

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

The goals of this project are:

1) Use conventional and developmental analysis 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 bio-oil environments

4) Determine the relationship between corrosion and the oxygenate concentration of bio-oils

5) Participate in round robin study comparing analysis results between four laboratories

Project Quad Chart Overview

Timeline

•Project started – Oct, 2010

•Duration – FY2018

Barriers

- Tt-E Pyrolysis of Biomass
- Materials Compatibility
- Conversion Technologies

Budget

- Total funding FY11 & FY12 - $320K
- Funding received in FY 2013 - $1,050K*
- Funding in FY 2014 - $1,250K
- Funding for FY 2015 - $1,675K**
- ARRA Funding - none

* Including three new tasks

** Including two additional tasks

Partners & Roles

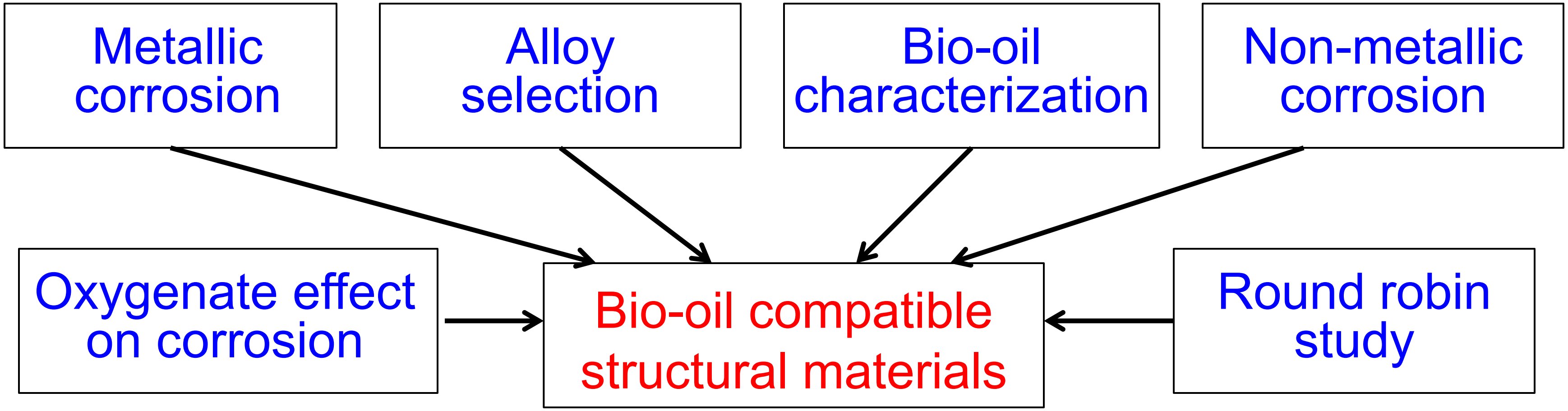
PNNL, NREL, Iowa State University, GTI, Virent, KiOR, VTT, RTI, Battelle-Columbus, USDA, Herty, Valmet/Fortum

• provide fluids for testing

• provide sites for exposing samples provided by ORNL

• provide exposed components from operating systems

Project Overview



- Characterize bio-oils to identify critical components and participate in round robin study of analysis techniques
- 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)
  - Utilize existing methods and develop new techniques as needed

- Characterization of actual component degradation from operating systems, field exposures of test materials, laboratory corrosion studies in bio-oils
  - Employ advanced electron microscopy and other material characterization techniques

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

Laboratory Corrosion Studies Are Used To Assess The Corrosivity Of Bio-Oils

- Samples of five structural alloys are exposed to bio-oil and to bio-oil vapors
- Corrosion coupons and stress corrosion U-bend samples are immersed and exposed in the vapor phase of each environment
- Exposure temperature is 50°C unless oils are "stabilized" to minimize polymerization
- Samples are examined after the first 250 hour exposure, after an additional 250 hours and again after another 500 hours for a total of 1,000 hours
- Stabilized bio-oils and/or oils with significantly reduced oxygen content can be tested in autoclaves at higher temperatures
- Have 8 rigs for atmospheric pressure studies & 2 autoclaves

Many Materials Exhibit Unacceptable Or Marginal Corrosion Rates (mm/y) at 50°C

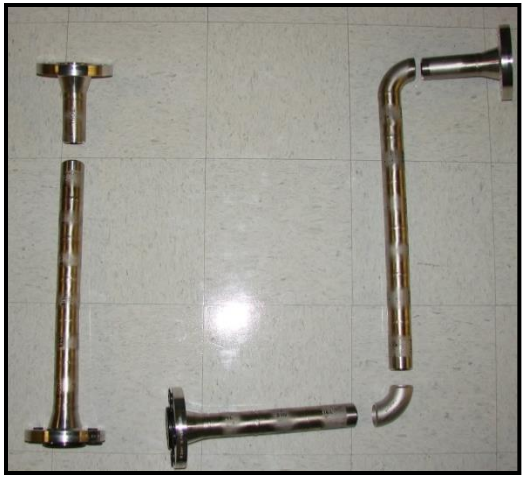
Time (hr)	Carbon Steel	2¼ Cr – 1 Mo	409 Stainless	304L Stainless	316L Stainless
USDA bio-oil derived from **switch grass** after 500 hours					
Above	0.23	0.36	<0.01	<0.01	<0.01
Immersed	0.62	1.44	0.82	<0.01	<0.01
VTT pyrolysis oil derived from **pine sawdust** after 500 hours					
Above	0.60	0.85	0.14	<0.01	<0.01
Immersed	2.93	4.09	0.35	<0.01	<0.01
Mix of fractions #3 and #4 ISU bio-oil derived from **corn stover** after 1,000 hours					
Above	1.16	1.57	0.15	<0.01	<0.01
Immersed	2.10	3.75	1.20	<0.01	<0.01
Aqueous fraction #5 derived from ISU **corn stover** after 1,000 hours					
Above	1.21	1.44	0.03	<0.01	<0.01
Immersed	1.28	1.81	0.67	<0.01	<0.01

Based on assumption that >0.25 mm/y (0.010 inches/y) is unacceptable and 0.10-0.25 mm/y (0.004-0.010 inches/y) is marginally acceptable

At 50°C, Corrosion Studies Show

- As produced bio-oils are very corrosive to common structural materials (carbon steel, 2¼Cr-1Mo steel and 409 stainless steel) because of the significant carboxylic acid content
- As-produced bio-oils are not corrosive to 300 series stainless steels like 304L and 316L (higher Ni and Cr, so more expensive)
- Reduction of oxygen content to ≤ 3.3% results in no corrosion of the low alloy materials even at temperature as high as 350°C – based on previous ORNL autoclave tests
- Laboratory corrosion studies are relevant to bio-oil storage and transport, but biomass liquefaction process equipment operates at higher temperatures and pressures
- Since exposure in actual operating systems is at much higher temperatures and pressures, ORNL is providing samples for exposure in operating systems and examining components and samples exposed for extended times in operating systems

Spool Pieces & Test Coupons Are Being Exposed In Operating Biomass Liquefaction Systems



Spool pieces fabricated from 6 different alloys and installed in NREL's pyrolysis system

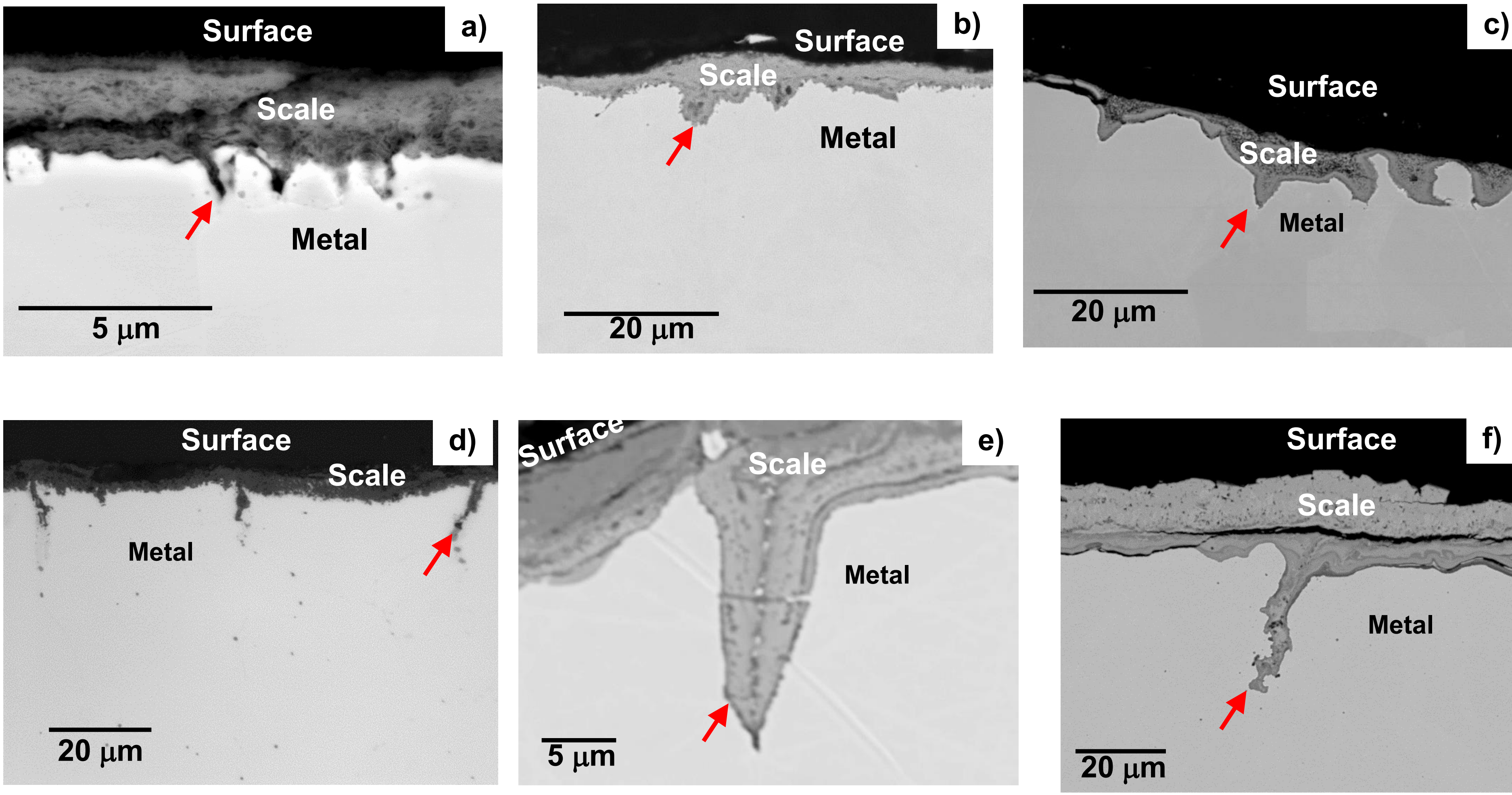
Spool piece fabricated from 6 different alloys and installed in GTI's system

Spool piece fabricated with 6 different alloys and installed in KiOR's operating system

Sample rack with coupons being exposed in freeboard area of ISU's fluidized bed pyrolysis system

- ORNL spool pieces and test coupons delivered to Iowa State, Virent, KiOR, GTI, NREL, PNNL & Valmet with plans to provide samples for other partners
- ORNL examining tubing and reactor components from partner commercial, pilot, and lab scale systems

Preferential Internal Oxidation Has Been Observed On Many 316L/H Samples

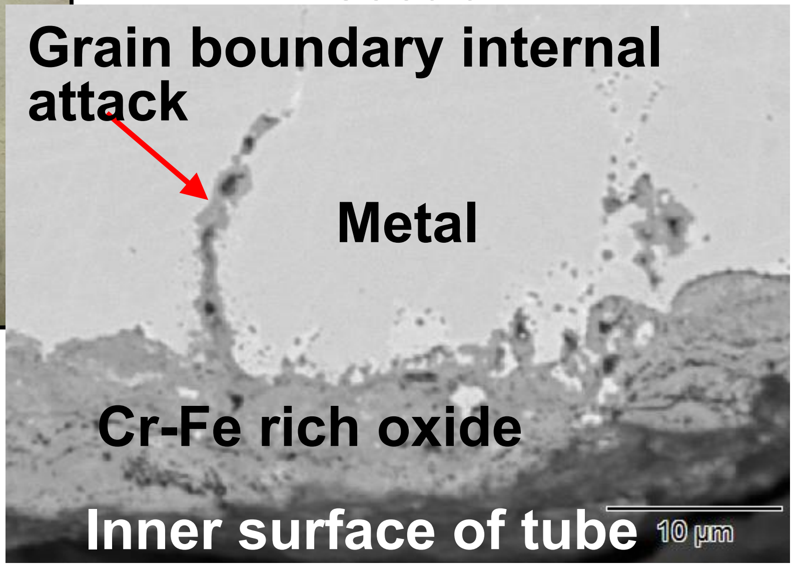


Exposure times 100-200 h for a & c and 600-100 hr for b & d

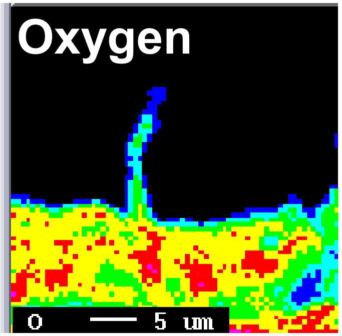
Preferential Attack Observed On 316L Pyrolyzer Component With >2000 h Exposure

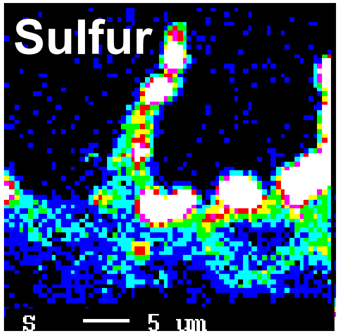
Component from VTT pyrolysis system

Scanning electron micrograph of cross-section



Microprobe maps





- Attach appears to be a result of internal sulfidation and oxidation
- Creates concern as to whether attack will grow deeper with time and/or serve as crack initiation sites
- Continuing effort to expose samples and/or acquire pyrolyzer components with longer exposure times to better assess this type of attack

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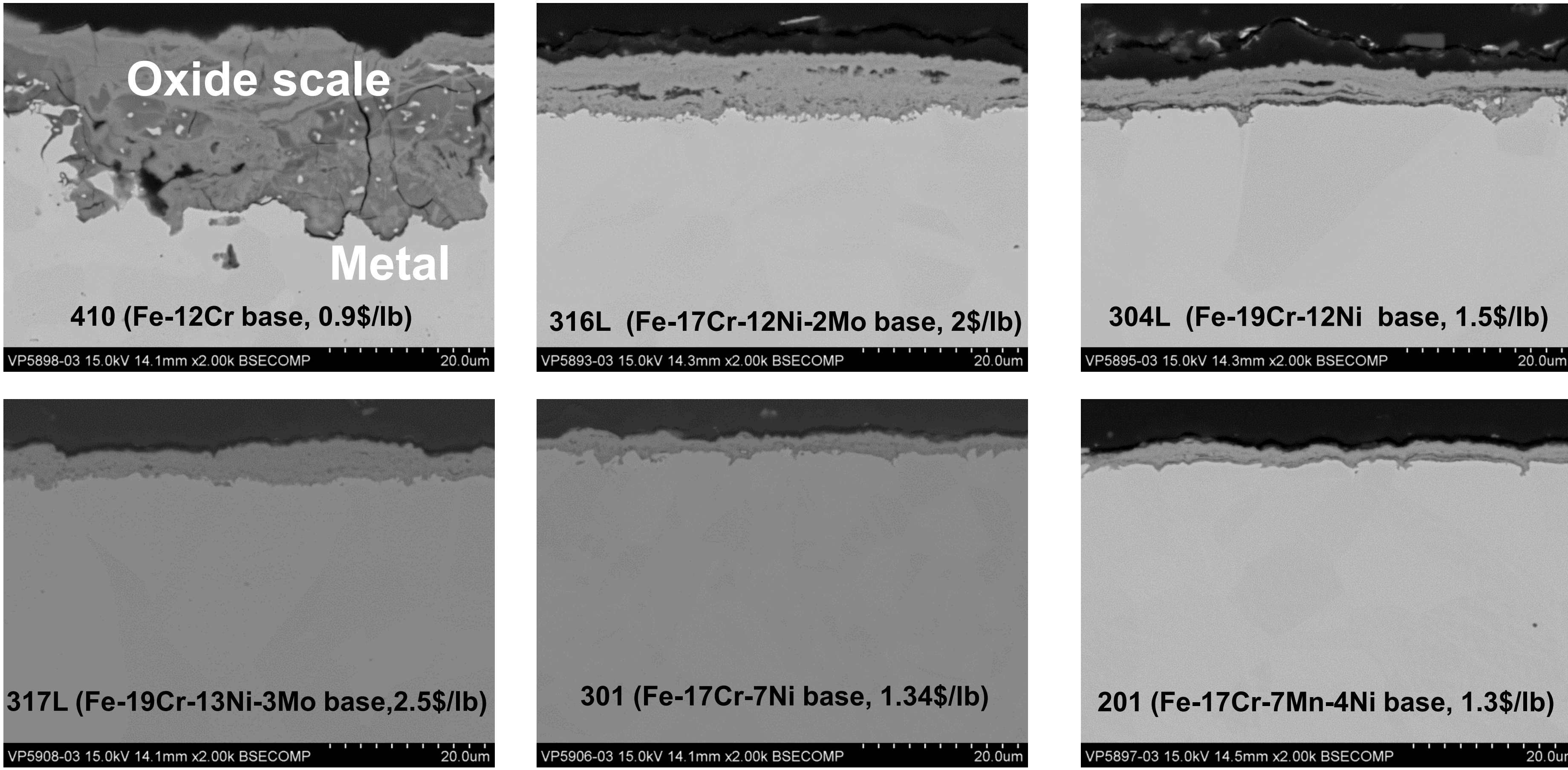
Results Of Alloy Exposures at Iowa State's Pyrolysis Process Development Facility

SEM cross-sections after 83 h (longer term exposure in progress)



High Mn, low Ni 201 stainless (less $) shows promise relative to 300 series

- have other indications of good resistance in multiple exposures
- need to determine if high Mn, low Ni provides better resistance to S

Technical Achievement – Polymer Compatibility

Nonmetallic Material Studies Conducted

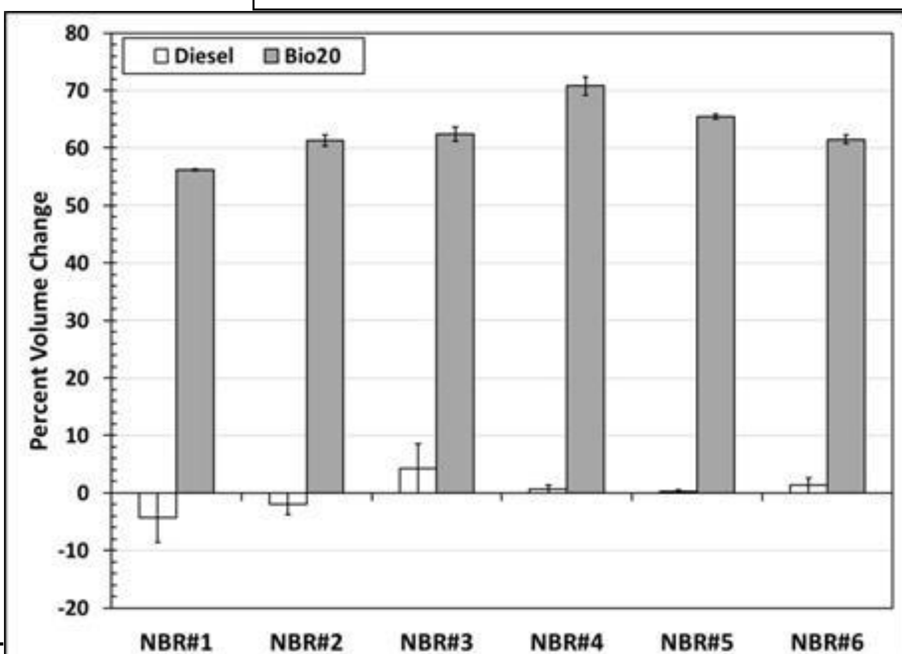
- Objective: evaluate compatibility of common infrastructure plastics and elastomers with bio-oil
  - Chemistry of bio-oil can vary widely with processing variables and feedstock
  - Bio-oils contain significant quantities of ketones, phenols and other oxygenates
- Solubility analyses to predict polymer compatibility of representative bio-oil
- Exposure study of elastomers and plastics with a Bio20 blend containing fast pyrolysis bio-oil
- Polymer compatibility is primarily dependent on solubility (not corrosion)

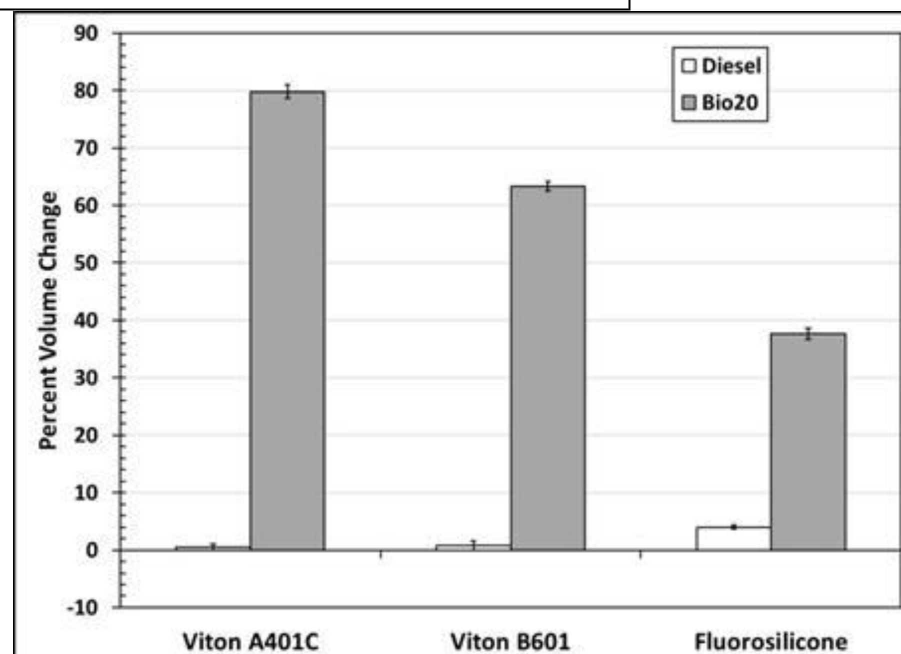
Photo showing polymer specimens mounted in exposure chamber

Results Showed Large Bio-Oil Effect On Elastomers

- Solubility analysis
  - Solubility parameters for bio-oil's primary components similar to each other, indicating this technique may be useful for different bio-oils
  - Predicted results corresponded to the observed volume change for most materials
  - Exceptions: fluoroelastomers (incompatible with ketones due to high kinetic diffusivity)
- Empirical study-Elastomers
  - Very high volume expansion observed for fluoroelastomers & acrylonitrile rubbers (NBRs)
  - Polyurethane and neoprene also exhibited pronounced swelling

Negligible changes were observed for off-road diesel (home heating oil), but the addition of 20% bio-oil caused high swell levels

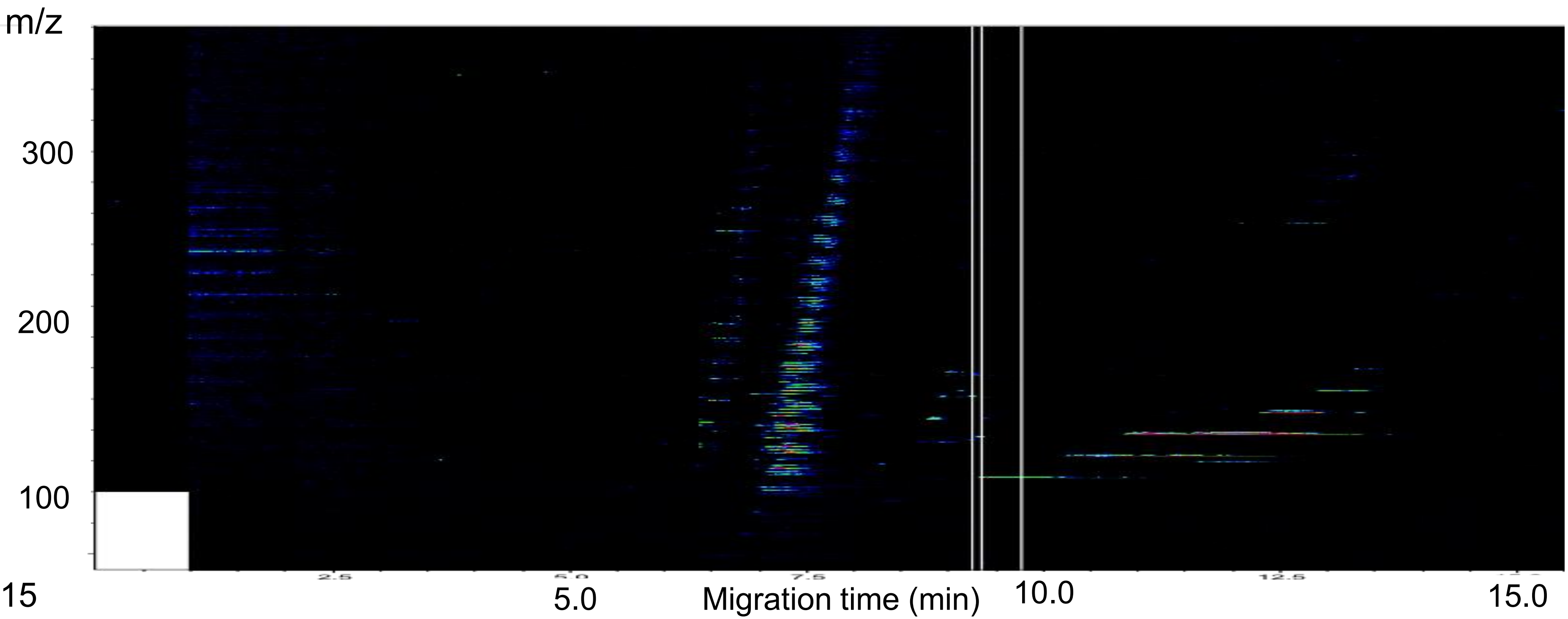




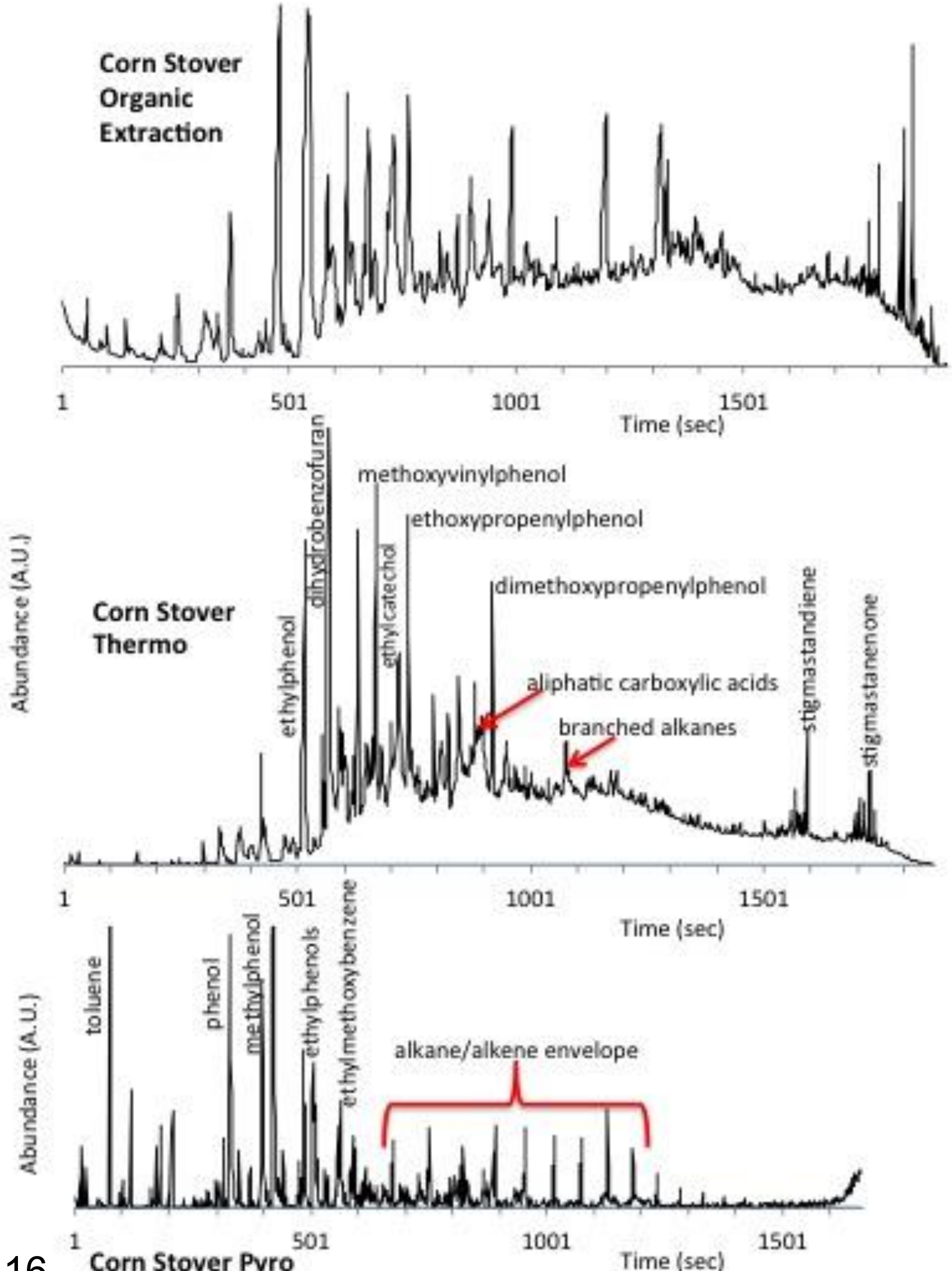
Technical Achievement – Chemical Characterization

CE-Electrospray Ionization Mass Spectrometry Provides Special Capabilities For Two Tasks

- Very unique capability shows wide, complex range of compounds
- The electropherogram below shows separation of the several groups of anionic oxygenated compounds ranging from simple carboxylic acids, dicarboxylic acids, and hydroxyl carboxylic acids to aromatic carboxylic acids
- This data indicates the source of these oxygenated species originates from both cellulose and lignin sources



Direct Sampling Provides More Information



Thermal Desorption/Pyrolysis GC-MS:

- Reveals energetically valuable material left behind on char
- Reduces sample biasing resulting from over-sampling of lighter plant oils with conventional solvent-extraction GC-MS methods
- Consequences if heavy oils are analytically under represented:
  - Disposal of energetically valuable residuals along with inorganic char
  - Underestimation of corrosivity of low % "sludge" deposits on infrastructure materials

Technical Achievement – Deoxygenation Effects

New Task Will Address Relationship Between Oxygenate Content And Corrosivity

- There is a need for a systematic study of bio-oil corrosivity as a function of the concentration of oxygen-containing compounds
- In this task, bio-oil samples will be hydrotreated to varying levels to reduce the oxygen content and then studied for corrosivity and concentration of oxygen-containing functional groups

  - Bio-oil samples are being acquired from at least three sources

  - Characterization and corrosion studies have been started

  - Arrangements made for hydrotreating samples
- Ultimately, this task should determine the extent of oxygenate removal necessary to make bio-oils much less corrosive

Round Robin Study Of Analytical Characterization Techniques Initiated

- Study led by Mariefel Olarte & others (PNNL/NREL/INL)
- ORNL joined as a participant in FY2015
- Identified and began preparing for four test methods
- Set to receive nine bio-oil samples
- Will perform four test methods on each sample:
  - *Total carbonyl*
  - *Water + carbonyl*
  - *Single dissolution solvent GC-MS for species survey*
  - *Acid/carboxylic acid number*

Relevance

- There are significant materials degradation issues with biomass-derived products due to oxygen-containing compounds
- **To meet the platform's production and cost goals it is essential that the least expensive structural materials with adequate corrosion resistance be identified**
- Project focuses on development of new analysis tools and identification/development of corrosion resistant materials **so materials durability issues don't prevent the successful commercialization of the most promising bio-oil production technologies**

Critical Success Factors

- Full characterization of biomass-derived oils and correlation with materials corrosivity
  - Different biomass sources yield differences in composition/properties of bio-oils so a wide range of materials/conditions need to be studied
  - Elucidate attack mechanisms and correlate with bio-oil components to guide future process optimization and materials selection
- Successful identification of metallic and non-metallic materials resistant to bio-oils derived from a wide range of biomass types is key measure of success for this project
- Note: there is not a “one shoe fits all” solution and materials will need to be selected on the basis of corrosion resistance, cost, fabricability, weldability, etc. for each process technology and biomass source

Future Work

- Continue to characterize bio-oils from multiple sources and correlate with corrosion of metallic and non-metallic materials
  - Perform chemical characterization of bio-oils
  - Develop new analysis techniques
  - Continue laboratory corrosion studies
  - Determine effect of oxygenate concentration on corrosion
  - Participate in round robin study of analysis techniques

- Continue efforts to examine actual service components and to expose candidate materials in operating systems
  - Provide corrosion samples for exposure in operating systems
  - Examine corrosion samples after exposure
  - Acquire and examine components from operating systems after exposure for extended service times

Summary

- **Project Approach**
- Characterize a range of bio-oils and the degradation of materials, identify alternate materials and apply/develop new analysis techniques
- **Technical Progress and Accomplishments**
- Observed consistent pattern of preferential internal attack of 316L SS and found evidence suggesting high Mn, low Ni alloys form less reaction product than alloys with higher Ni content
- Continued development of analytical techniques
- **Project Relevance**
- Low-cost materials compatible with bio-oils needed for commercialization
- **Critical Success Factors**
- Elucidate attack mechanisms and correlate with bio-oil components to guide future process optimization and materials selection
- **Future Work**
- Continue development of analytical techniques, expose samples in operating systems, examine system components, continue laboratory corrosion studies, relate oxygenates to materials degradation, identify suitable materials
- **Technology Transfer and Collaborations**
- Multiple external collaborations, multiple conference presentations

Additional Slides

Response to Previous Reviewers' Comments

- The previous review was conducted in May, 2013, and there were two areas identified by reviewers that we needed to address – study a broader range of bio-oils and more industrial involvement

Response – we have been able to acquire and characterize bio-oils from a significant number of suppliers – Virent, KiOR, Battelle-Columbus, Technical Research Centre of Finland (VTT), Gas Technology Institute, University of Georgia, Canmet, and Ensyn in addition to the original suppliers.

Industrial participation in our project has also increased and includes the companies listed above as well as Valmet/Fortum and Herty Advanced Materials Development Center (Georgia Southern University).

Responses to Previous Reviewers' Comments

- A comment prior to the May 2013 review noted that we need to maintain an effort to stay aware of the progress being made in Europe

  Answer – During this past 2 years we made invited presentations at conferences in Finland and Brazil, and we published in a journal that serves the Canadian pulp and paper industry. We are collaborating with researchers at the Technical Research Centre of Finland who are leaders in biomass pyrolysis studies in Europe. We also provided corrosion samples for exposure in the industrial scale biomass pyrolysis system in Joensuu, Finland.

Open Literature Publications

- "Corrosion Considerations for Thermochemical Biomass Liquefaction Process Systems in Biofuel Production", M.P. Brady, J.R. Keiser, D.N. Leonard, L. Whitmer and J.K. Thomson, *JOM*, Vol. 66, No. 12, 2014.
- "Degradation of Structural Alloys In Biomass-Derived Pyrolysis Oils", James R Keiser, Michael P Brady, Raynella M Connatser and Samuel A Lewis, Sr, *Journal of Science & Technology for Forest Products and Processes*, Vol. 3, No. 3, pg 16-22, 2013.
- "Measuring Bio-Oil Upgrade Intermediates and Corrosive Species with Polarity-Matched Analytical Approaches", Raynella M Connatser, Samuel A Lewis, Sr., James R Keiser and Jae Soon Choi, *Biomass and Bioenergy*, Vol 70, pg 557-63, November 2014.

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Publications and Presentations

- “Bio-Oil Properties and Effects on Containment Materials, James R Keiser, Michael P Brady, Jeffery K Thomson, Raynella M Connatser, Samuel A Lewis, Sr, and Donovan N Leonard, NACE International Corrosion 2014, March 10-13, 2014, San Antonio TX.
- “Corrosion Considerations In Selection Of Structural Materials For Thermochemical Processing Of Biomass”, James Keiser, Michael Brady, Sam Lewis, Sr., Raynella Connatser, Jeffery Thomson and Donovan Leonard, 2014 International Chemical Recovery Conference, June 8-12, 2014, Tampere, Finland.
- “Impact Of Corrosion On Selection Of Structural Materials For thermochemical Processing Of Biomass”, James R Keiser, Michael P Brady, Samuel A Lewis, Sr, Raynella M Connatser, Donovan N Leonard, Lysle E Whitmer and Patrick A Johnson, 2014 TAPPI PEERS conference, September 15-17, 2014, Tacoma WA.

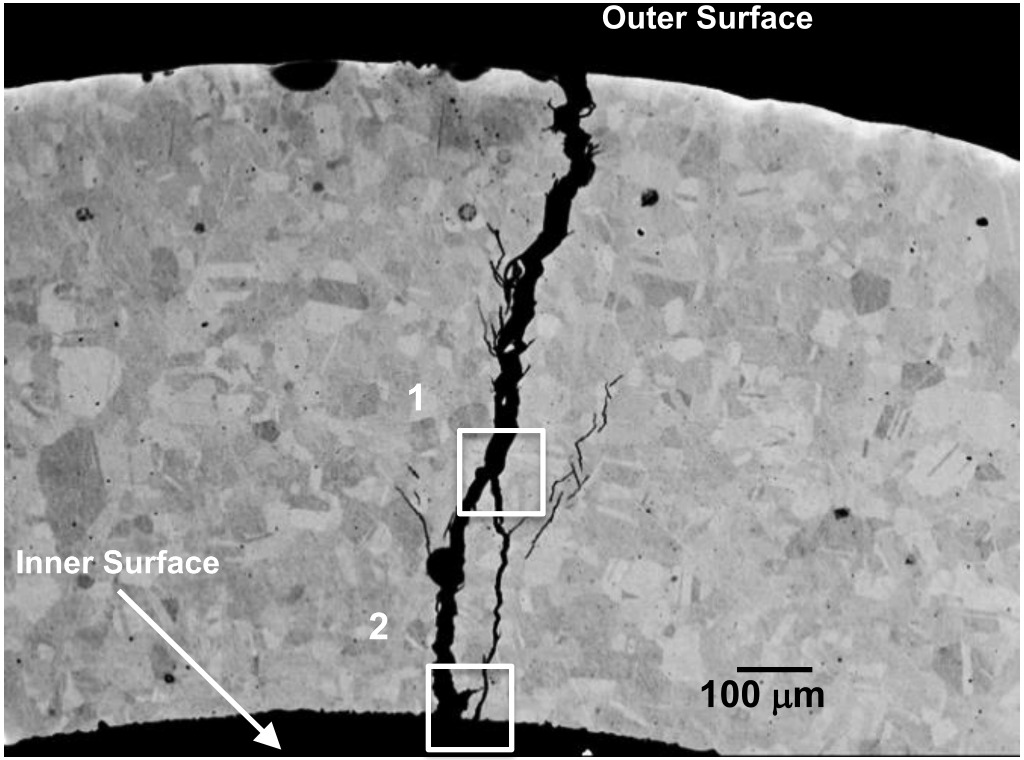
Presentations (without publications)

- Invited - “Degradation Of Structural Alloys In Biomass-Derived Pyrolysis Oil” James Keiser, Michael Brady, Raynella Connatser and Samuel Lewis, Sr, 8th International Colloquium Black Liquor and Biomass to Bioenergy and Biofuels, Belo Horizonte, Brazil, May 19-23, 2013
- “Corrosion Issues Associated With Thermochemical Production Of Biofuels”, James R Keiser, Michael P Brady, Samuel A Lewis, Sr and Raynella M Connatser, tcbiomass2013, Chicago, September, 2013
- “Corrosion Studies With Biomass-Derived Fuels, James Keiser, Michael Brady, Samuel Lewis, Sr, Raynella Connatser, Jeffery Thomson and Patrick Johnston, MS&T Conference, Pittsburgh, October, 2014
- Invited – “Corrosion Issues In Bio-Oil Production”, James Keiser, Michael Brady, Samuel Lewis, Sr, Raynella Connatser and Donovan Leonard, University of Toronto Annual Research Review meeting, November 12, 2014
- Invited – “Materials Selection For Biomass Thermochemical Liquefaction (And Gasification)” by James Keiser, Michael Brady, Samuel Lewis, Sr., Raynella Connatser and Donovan Leonard, Georgia Institute of Technology’s Renewable Bioproducts Institute symposium, November 14, 2014.

Interdisciplinary ORNL Team from Materials Science & Technology and Energy & Transportation Science Divisions

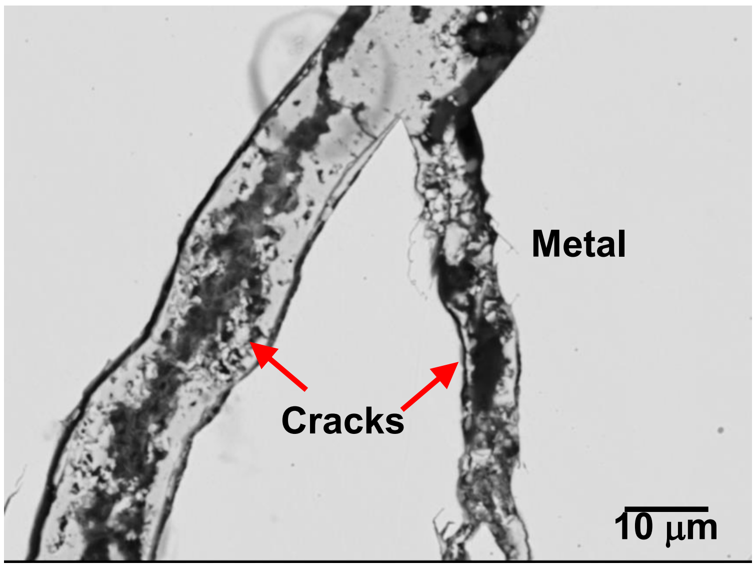
- Project PI – Jim Keiser
- Bio-Oil Compatibility-Task Leader – Jim Keiser
- Alloy Materials-Task Leader – Mike Brady
- Bio-Oil Characterization-Task Leaders – Sam Lewis and Maggie Connatser
- Non-Metallic Materials-Task Leader – Mike Kass
- Oxygenate Effect On Corrosion-Task Leader – Jim Keiser
- Round Robin Study-Task Leaders – Maggie Connatser and Sam Lewis

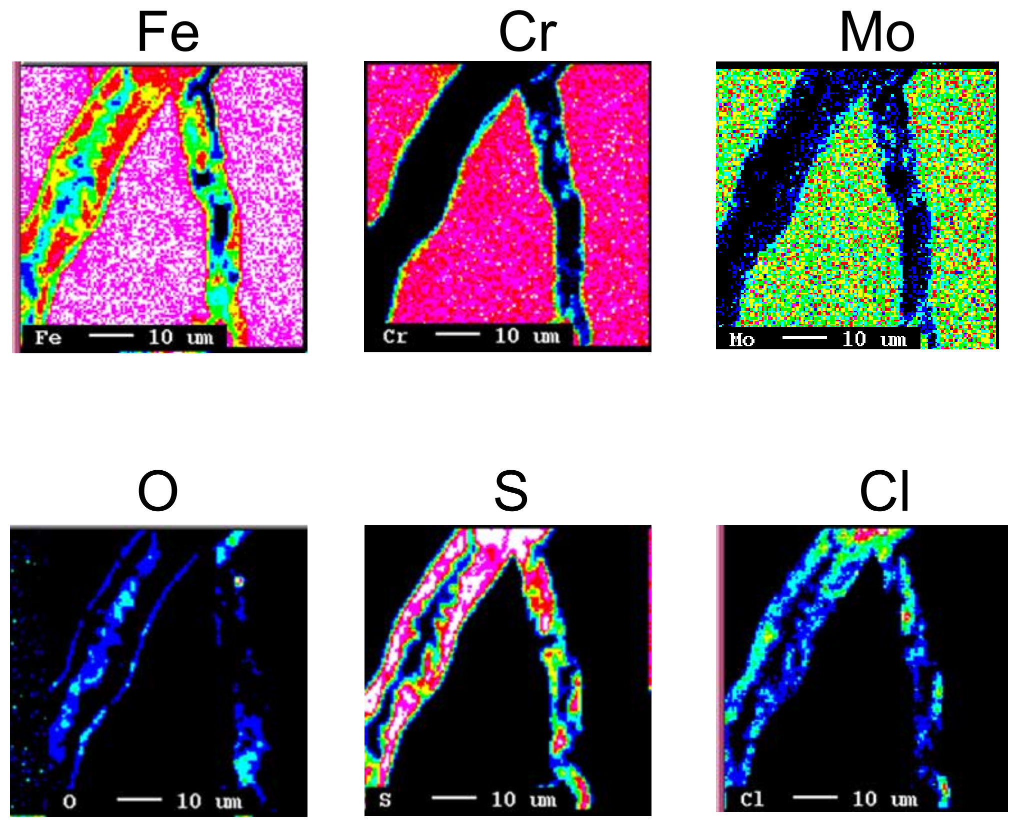
A 316L Stainless Steel Tube That Cracked After Exposure To Off-Normal Operating Conditions Was Examined



The electron microprobe was used to determine the elemental distribution in the crack and in the surface around the crack

Significant Concentrations Of S And Cl Were Found In the Crack





Relative intensity increases from black to blue to green to yellow to red to white

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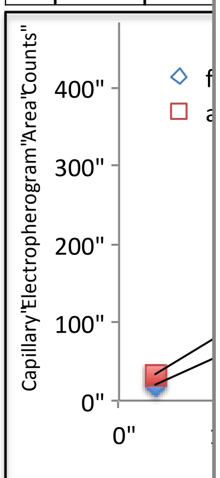
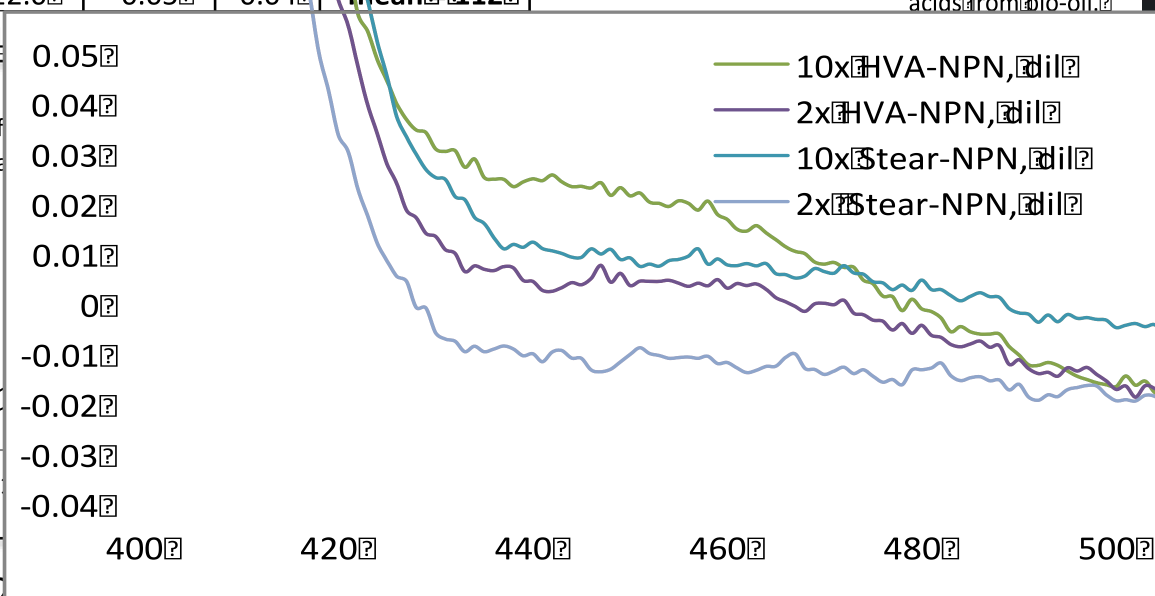
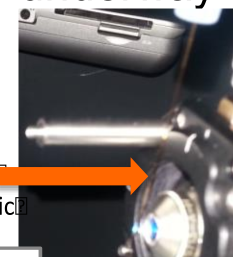
Enhancing Reproducibility And Sensitivity

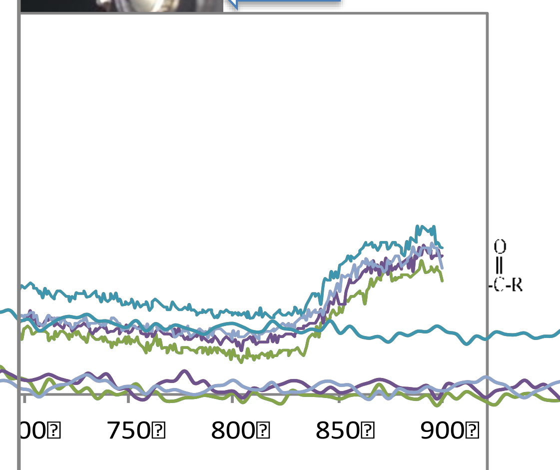
- Progress in developing tailored extractions & separation-detection approaches for more quantitatively representative, qualitatively accurate bio-oil characterization
- Carboxylic acid derivatization for aqueous separation platform with laser-induced fluorescence (LIF) detection selectively improves sensitivity in bio-oil assessment and corrosive component characterization
- Organic oxygenate extracts from real bio-oils have been derivatized; separations of complex mixture containing now-fluorescent carboxylic acids underway

Sample	ModTAN	Abs Dev	%RSD	
Aliquot 1	109.3	2.65	2.37	**Avg RSD = 1.18**
Aliquot 2	114.4	2.45	2.19	**n = 4**
Aliquot 3	112.0	0.05	0.04	**mean = 112**
Aliquot 4	11			









Reproduc… modified TAN and CE.

…oxylic acid, derivatized by … orptivity than the benchmark … faced to capillary for aqueous-platform separation of derivatized carboxylic acids from bio-oil