2017 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Materials Degradation In Biomass-Derived Oils

2.4.2.301

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Bio-Oil Technology Area Review

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ORNL is managed by UT-Battelle
for the US Department of Energy

Goals/Objectives

The presence of significant concentrations of oxygen-bearing compounds, particularly carboxylic acids and other carbonyl-containing compounds, makes biomass derived oils corrosive to many 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) Determine the relationship between corrosion and the oxygenate concentration of bio-oils

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

5) Develop a test method for assessing the corrosivity of bio-oils

6) *Identify or develop materials specifically suited for use in bio-oil production, processing, storage and transporting environments*

Quad Chart Overview

Timeline

- Project start date – Oct., 2010
- Project end date – Sept., 2018
- Percent complete - ~75%

Budget

	Total Costs FY 12-14 (K$)	FY 15 Costs (K$)	FY 16 Costs (K$)	Total Planned Funding (FY 17-Project End Date)
DOE Funded	$2,513	$1,675	$1,600	FY17 planned $1,600K FY17 revised $1,000K FY18 planned $1,600K
Project Cost Share (Comp.)	Only receiving informal in-kind support from the extensive group of partners			

Barriers

- Tt-E Pyrolysis of Biomass
- Ct-S Materials Compatibility & Reactor Design

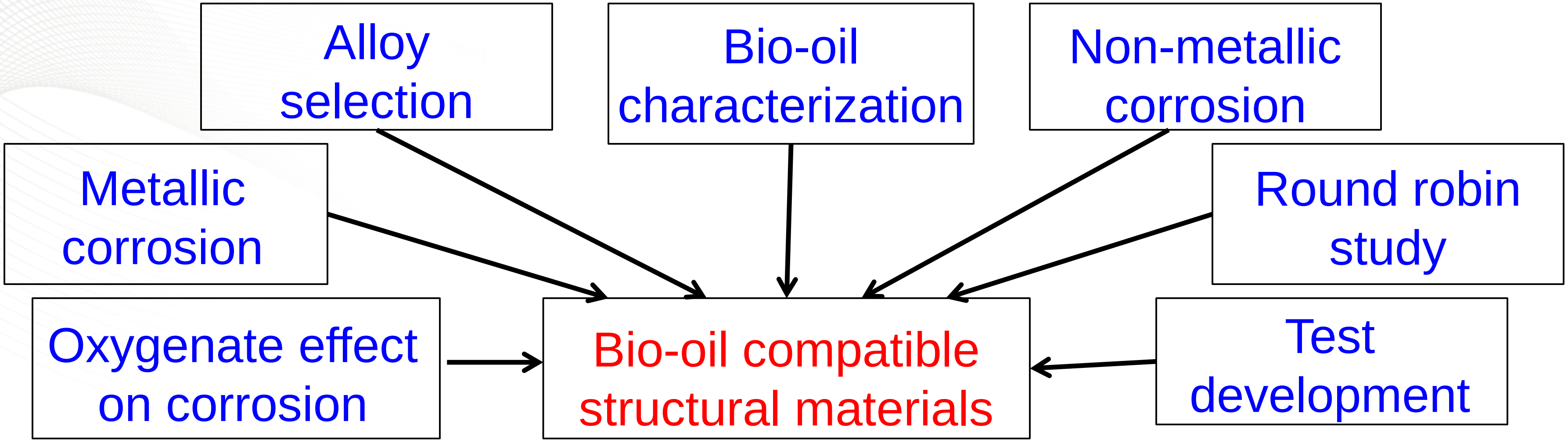
Partners

NREL, Iowa State Univ, Michigan State Univ, PNNL, GTI, VTT, Battelle, CanmetENERGY, FPInnovations, Univ of Toronto, Aarhus Univ, Valmet, Fortum + several recent contacts

These partners and others:

- Provide fluids (raw and hydrotreated) for testing
- Provide sites for exposing samples provided by ORNL
- Provide exposed components from operating systems

Project Overview



Alloy selection

Bio-oil characterization

Non-metallic corrosion

Metallic corrosion

Round robin study

Oxygenate effect on corrosion

Bio-oil compatible structural materials

Test development

- Characterize bio-oils to identify critical components, develop new test methods and participate in round robin study of analysis techniques
- Characterize the degradation of metallic and non-metallic materials by raw and treated biomass derived bio-oil
- Determine the mechanism(s) responsible for degradation of potential structural materials used in biomass pyrolysis systems
- Develop test method to determine corrosivity of bio-oils
- Identify and/or develop materials compatible with bio-oil storage and transport (≤50°C) and production and processing (≥350°C) so that materials issues do not prevent successful commercialization of any bio-oil production technology

Approach (Management)

- All supported participants are staff members in ORNL’s Materials Science & Technology Division or Energy & Transportation Science Division
- ORNL staff members interact by phone, e-mail and in person on almost daily basis – hold informal meetings as needed
- ORNL staff members collaborate on publications and presentations
- Extensive number of organizations are partners who provide sample exposure sites, bio-oil samples, exposed components and/or project guidance
- Communicate with these project partners through phone and e-mail as well as face-to-face meetings at conferences, workshops, review meetings and on-site visit
- Communicate results through technical publications, conference presentations and visits to sites of interested parties

Approach (Technical)

- 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 samples and degraded components from <u>operating systems</u>, <u>field exposures</u> of test materials, and <u>laboratory corrosion tests</u> of candidate structural materials
  - Employ light microscopy as well as advanced electron microscopy and other material characterization techniques
- Identify or develop alternate materials with sufficient resistance to degradation. Analysis will focus on <u>lowest cost materials</u> that meet goals
- Technical success based on
  - Assessment and determination of degradation mechanism(s)
  - Successful identification of sufficiently low cost degradation resistant materials to enable advancement of bio-oil technologies to the commercialization stage

Laboratory Corrosion Studies Are Screening Test 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
Fast pyrolysis **untreated** bio-oil derived from pine sawdust after 1,000 hours					
Above	0.44	0.25	<0.01	<0.01	<0.01
Immersed	0.59	1.09	<0.01	<0.01	<0.01
Fast pyrolysis pine derived bio-oil **hydrotreated** to 2.9% oxygen after 250 hours					
Above	0.02	<0.01	<0.01	<0.01	Not tested
Immersed	0.09	0.06	<0.01	<0.01	Not tested
Aqueous fraction from pine derived bio-oil hydrotreated to 2.9% oxygen after 1,000 hrs					
Above	<0.01	<0.01	<0.01	<0.01	<0.01
Immersed	0.10	0.11	<0.01	<0.01	<0.01
Fast pyrolysis untreated bio-oil derived from guayule after 250 hours					
Above	0.57	0.71	<0.01	<0.01	<0.01
Immersed	0.80	2.23	0.82	<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

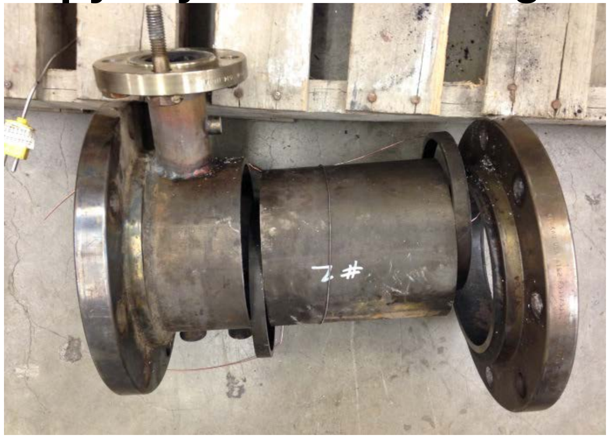
At 50°C, Corrosion Studies Show

- 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, at 50°C, are not corrosive to 300 series stainless steels like 304L and 316L (higher Ni and Cr, so more expensive)
- A significant reduction in the oxygen content of bio-oil results in considerably less or no corrosion of the low alloy materials
- Laboratory corrosion studies are relevant to bio-oil storage and transport and serve as a screening test, but biomass liquefaction process equipment operates at higher temperatures and pressures
- In order to collect information on material performance in actual operating systems 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

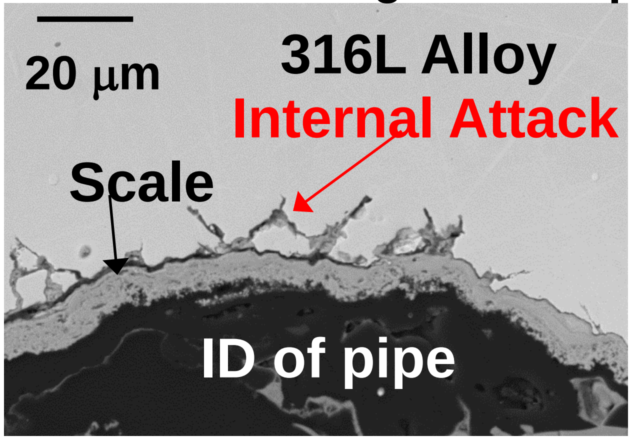
Technical Achievement – Field Corrosion Studies

Characterization of Alloys And Components From Operating Biomass Liquefaction Systems

316L pyrolysis reactor segment



SEM cross-section image 500 h operation

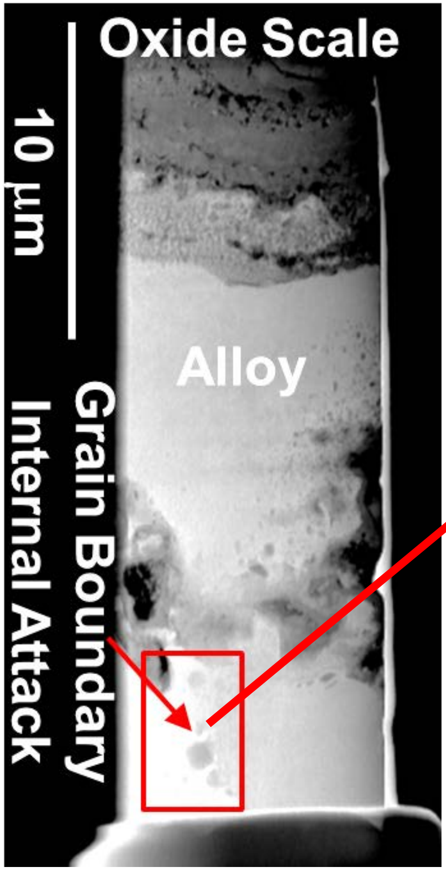


See internal attack in conventional stainless steels after short-term exposures
This attack has been observed in multiple systems/wide range of conditions
Evaluating range of Fe-Cr-Ni alloys: understand attack & guide alloy selection

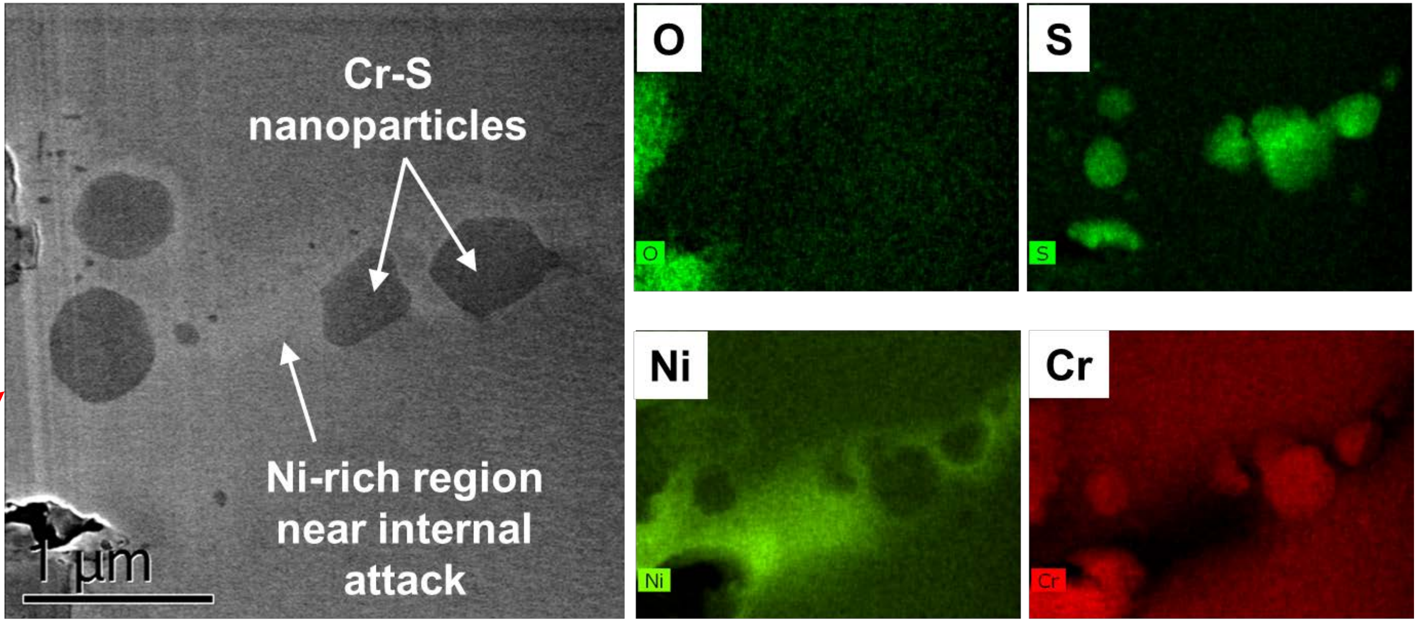
Alloy coupons and spool piece for exposure in biomass liquefaction systems

Advanced Electron Microscopy Helps Understand Local Nature Of The Internal Corrosion Attack

2000 h+ 316L stainless steel pyrolyzer operation: cross-section Focused Ion Beam lift-out of internal attack zone for analysis



STEM Image and Elemental Maps

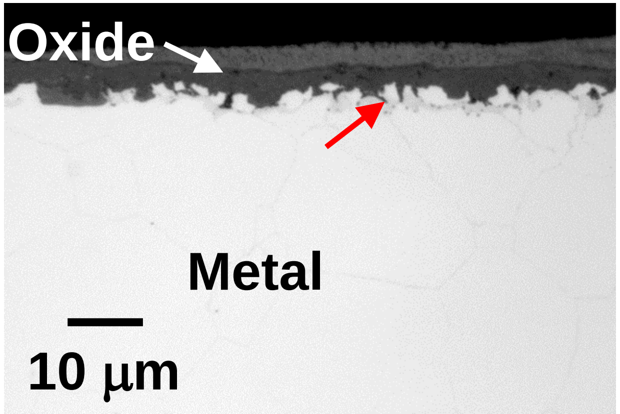


Internal attack regions locally enriched in nickel (Ni); chromium (Cr) used for corrosion protection via external Cr-oxide scale tied up by sulfur (S) instead

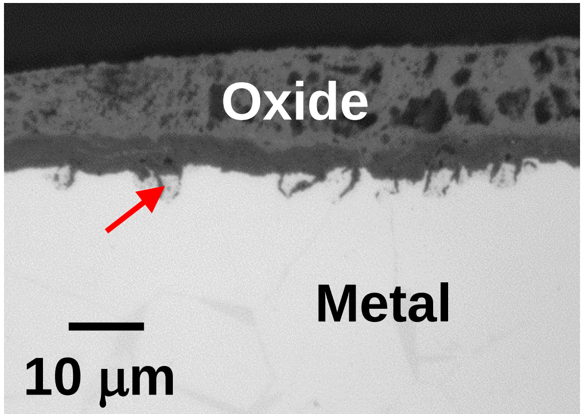
Low Cost 201 Stainless Shows Promise for Better Corrosion Resistance than 304L & 316L

SEM cross-sections of samples after ~100 h in hydrotreated bio-oil + vacuum gas oil co-processing in Davison Circulating Riser

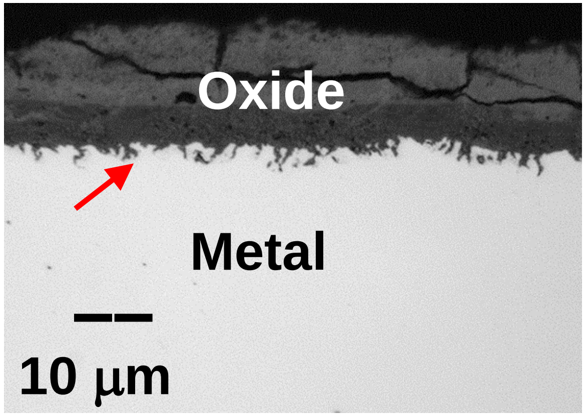
201 (Fe-17Cr-5Ni-7Mn)



304L (Fe-18Cr-10Ni)



316L (Fe-17Cr-12Ni-2Mo)



- Better short-term corrosion resistance for 201 also seen in other biomass liquefaction relevant environments (longer term exposures in progress)
- Low Ni, high Mn in 201 may aid resistance if sulfur is a key contributor to attack
- 201 lower cost: ~\$1.3/lb for 201 vs. ~ 1.5/lb for 304L and ~ \$2/lb for 316L

Technical Achievement – Non-Metallic Corrosion Studies

Compatibility Of Key Infrastructure Elastomers And Plastics Evaluated

Elastomers	Application	Plastics	Application
Fluorocarbons (8 types)	Seals (o-rings, gaskets, etc.)	HDPE (high density polyethylene)	Structural piping material
NBR (acrylonitrile butadiene rubber) (6 types)	Seals (o-rings, gaskets, etc.) Fuel hoses	Polypropylene	Limited use in tanks and pumps
Silicone rubber	Seals (o-rings, gaskets, etc.)	POM (polyoxymethylene, also known as acetal) (2 types)	Fuel lines and tank components
Fluorosilicone	Seals (o-rings, gaskets, etc.)	Nylon (4 types)	Permeation barrier and seal material
Neoprene	Seals (o-rings, gaskets, etc.)	PVDF (polyvinylidene fluoride)	Fuel permeation barrier for piping
SBR (styrene butadiene rubber)	Fuel hose cover	PTFE, also known as Teflon (polytetrafluoroethylene)	Fuel permeation barrier for piping and seal material
Polyurethane	Coatings	PPS (polyphenylene sulfide)	Fuel permeation barrier for piping
NBR/cork	Gaskets	PET (polyethylene terephthalate or Mylar) (2 types)	Fuel permeation barrier for piping
Epichlorohydrin rubber/cork	Gaskets	PBT (polybutylene terephthalate)	Limited use in fuel supply systems
		PTU (polythiourea)	Fuel system coating material
		Isophthalic polyester resins (2)	Fiberglass tank and piping resin
		Terephthalic polyester resin	Fiberglass tank and piping resin
		Novolac vinyl ester resin	Fiberglass tank and piping resin

Studies Of Non-Metallic Materials Have Produced Valuable Information

- Only recognized study that has:
  - Evaluated infrastructure plastics (including fiberglass resins)
  - Evaluated vapor-phase compatibility
- Fuel types evaluated include:
  - Baseline petroleum distillate (diesel)
  - Fast pyrolysis bio-oil
  - Upgraded and hydrotreated bio-fuel
- Results have shown areas of concern (fluorocarbons) and areas of opportunity (low-cost silicone rubbers)
- Ketones and other carbonyl compounds identified as likely cause of some degradation
- Work has resulted in 3 journal-level publications
- Recognized by industry for leadership in polymer-fuel compatibility evaluation

Top down view of specimens placed inside exposure chamber.

Property measurements include change in volume, hardness and mass before and after drying

Technical Achievement – Chemical Characterization Studies

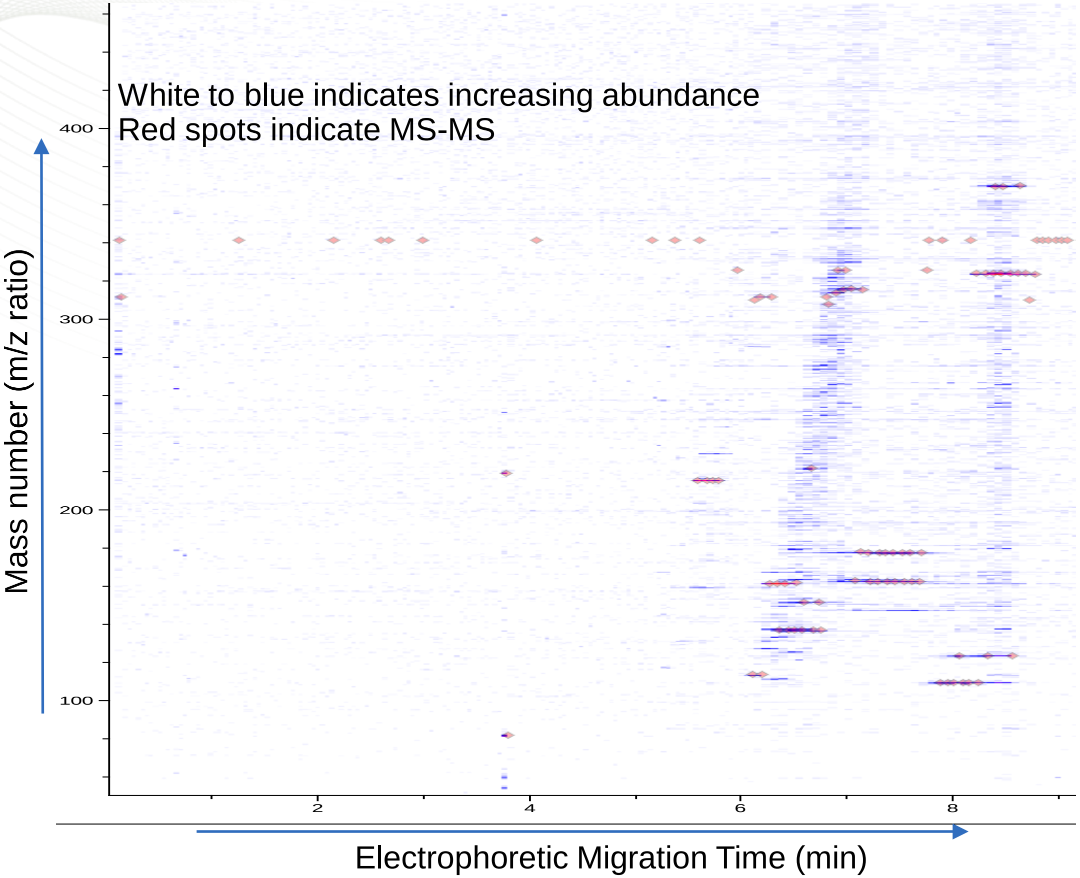
Measurements Of Acidity Have Been Made On All Bio-Oils Evaluated In Corrosion Tests

Bio-Oil Source	Condition	AMTAN* (mg KOH/g)	Formate (ppm)	Acetate (ppm)
Fast pyrolysis of pine sawdust	As produced	41	428	346
Fast pyrolysis of pine sawdust	Hydrotreated to 2.9% oxygen	8	<50	86
Fast pyrolysis of pine sawdust	Hydrotreated to 1.2% oxygen	5	<50	<50
Fast pyrolysis of guayule	As produced	76.5	940	2088

* Total Acid Number as measured using an aqueous extraction technique to recover water soluble compounds

Technical Achievement – Chemical Characterization Studies

Detecting Larger, Potentially Corrosive Oxygenates from Bio-Oil: CE-ESI-MS-MS

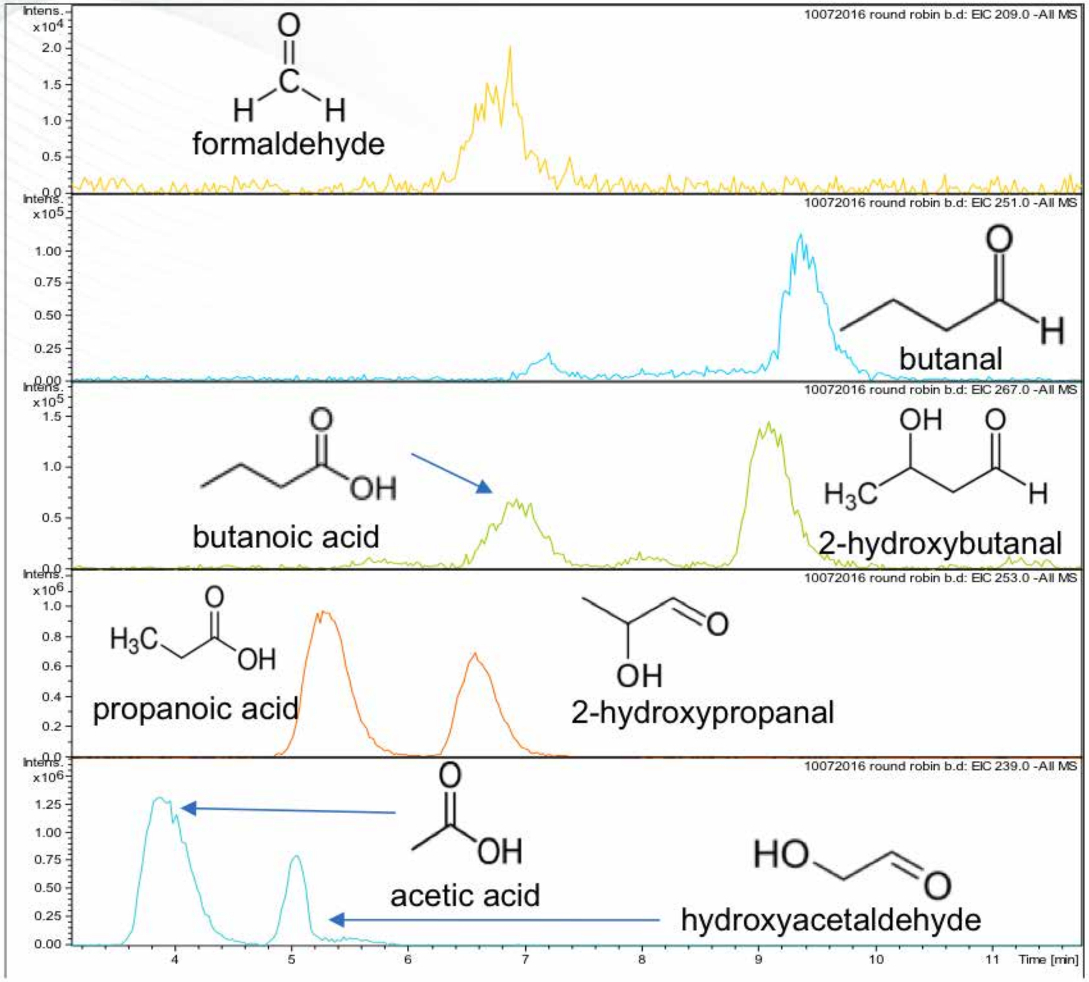


- Capillary Electrophoresis-Electrospray Ionization-Mass Spec-Mass Spec is a water-amenable separation platform which allows the separation and identification of small and large ionic compounds.
- The combination is being used to assess potentially corrosive carboxylic acids from lignin, sugars, and possible degradation of other oxygenates.

As CE is an aqueous separation platform, several families of possibly corrosive oxygenates are detectable:

- Cellulose-derived acids: furoic, glucuronic, and succinic
- Common lignin-derived compounds: vanillin, hydroxybenzabldehyde, hydroxybenzoic acid, vanillic acid, ferulic acid, guaiacol, and methyl guaiacol
- Sugar-derived acids, larger glucanic acids, and anhydrosugars, including levoglucosan

Detecting Larger, Potentially Corrosive Oxygenates from Bio-Oil: HPLC-ESI-MS-MS



- High Performance Liquid Chromatography-Electrospray Ionization-Mass Spec-Mass Spec is being used to assess potentially corrosive carboxylic acids alongside their hydroxyaldehyde counterparts

- Data shown laid groundwork for an on-going study of a bio-oil series prepared by HTL then catalytically upgraded at PNNL.

- This method is complementary to CE-MS-MS discussed earlier in that it offers a side-by-side look at structurally similar acids and non-acidic carbonyls.

Technical Achievement – Characterization Techniques

Round Robin Study Of Analytical Characterization Techniques Initiated

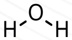
- Study led by Olarte & Padmaperuma (PNNL) & Ferrell (NREL)
- ORNL joined as a participant in FY2015
- Identified and evaluated 9 test methods over 2.5 years of performance
  - Titrations for total acid, carboxylic acids, carbonyls
  - P-31 and C-13 nuclear magnetic resonance
  - Chromatography (conventional GC-MS & HPLC-UV/vis) for select compound assessment
  - Iron leaching test for bio-oil (ORNL developed)
- Request granted to form ASTM working group on successful method, carbonyl titration (NREL lead: Christiansen)

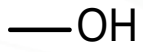
Technical Achievement – Deoxygenation Effects

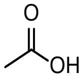
Task Is Addressing Relationship Between Oxygenate Content And Corrosivity

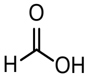
- There is a need for a systematic study of bio-oil corrosivity as a function of the concentration of oxygen-containing compounds
- In this task, bio-oil samples are being hydrotreated to varying levels to reduce the oxygen content and then studied at ORNL for corrosivity and oxygenate content
  - Bio-oils from one set of hydrotreated samples have been studied
  - Characterization and corrosion studies have started on second set of samples
  - Arrangements for third set of hydrotreated samples suspended due to reduction in project funding
- The ultimate goal of this task is to determine the extent of oxygenate removal necessary to make bio-oils much less corrosive

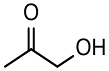
Oxygenates Of Interest For Systematic Evaluation/Corrosion Testing

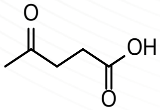

water

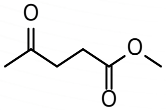

methanol

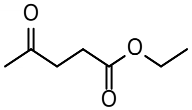

acetic acid

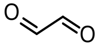

formic acid

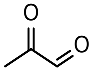

hydroxy-acetone

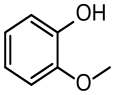

levulinic acid

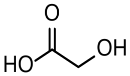

methyl levulinate

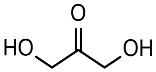

ethyl levulinate

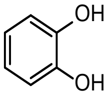

glyoxal

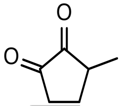

methyl glyoxal

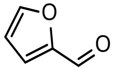

guaiacol

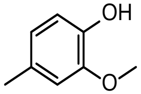

glycolic acid

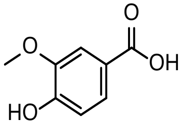

dihydroxy-acetone

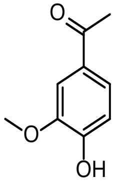

catechol

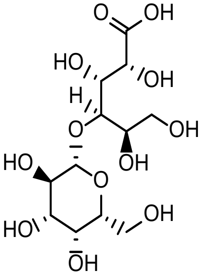

3-methyl-1,2-cyclopentanedione


furfural


creosol


vanillic acid

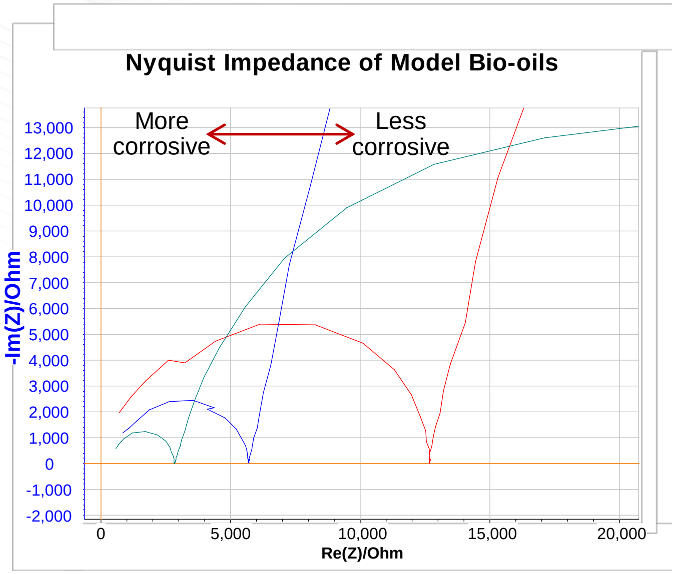

apocynin

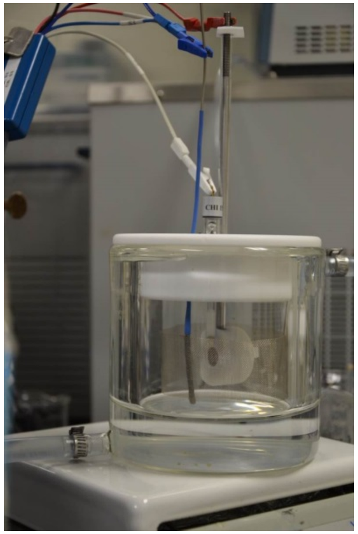

lactobionic acid

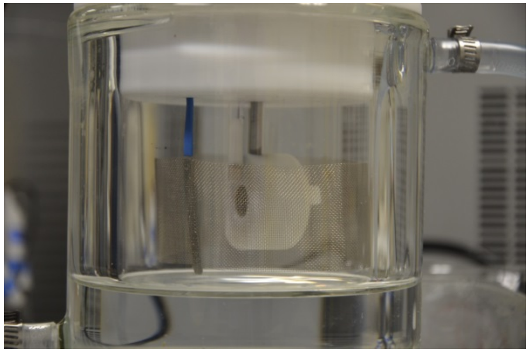
- A mixture of these oxygenates has successfully been made, and corrosion tests and screening are underway
- Because of the limited availability of hydrotreated bio-oils, this provides a means for a systematic study of the effect on corrosion behavior of oxygenates present in bio-oil

Technical Achievement – Test Development

Electrochemical Impedance Spectroscopy Has Potential As A Corrosion Test Method







The equipment shown is used for current testing to assess the potential for EIS to quickly evaluate the effects of different oxygenates on corrosion of metals

EIS can measure charge transfer resistance of metal or alloy of interest, and thus corrosion rate, with respect to time

- Corroding systems can show different impedance graphs depending on the nature of the corrosion mechanism
- Corroding interface (i.e. solution, metal/alloy, oxides, and corrosion products) can be modeled as an equivalent circuit. Measurement of the impedance of the system over a wide frequency range and fitting the data with an equivalent circuit, permits determination of the corrosion rate over time.

Relevance

- There are significant materials degradation issues with biomass-derived products due to oxygen-containing compounds; particularly acids, ketones and aldehydes
- **To meet the platform's production and cost goals it is essential that the <u>least expensive</u> structural materials with adequate corrosion resistance be identified**
- Project focuses on development of <u>new analysis tools</u> and <u>identification/development of corrosion resistant materials</u> so that 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, 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; special interest in HTL bio-oil and oil from algal feedstocks
  - Develop new analysis techniques
  - Continue laboratory corrosion screening studies
  - Determine effect of oxygenate concentration on corrosion
  - Participate in round robin study of analysis techniques
  - Communicate results through papers, presentations and meetings

    - In the last two years – 9 publications, 9 presentations, 5 posters
- Continue efforts to examine actual service components and to expose candidate materials in operating systems
  - Provide corrosion samples for exposure in operating systems; especially HTL
  - Examine corrosion samples after exposure
  - Determine resistance of low-Ni, high Mn alloy to intergranular attack
  - Acquire and examine components from operating systems after exposure for extended service times – special interest in components exposed to algal oil

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

- **Technology Transfer and Collaborations**

- Multiple external collaborations, multiple conference presentations

Additional Slides

Open Literature Publications

- “Compatibility Assessment of Elastomeric Infrastructure Materials with Neat Diesel and a Diesel Blend containing 20 Percent Fast Pyrolysis Bio-Oil”, Michael D Kass, Chris Janke, Raynella Connatser, Sam Lewis, James Keiser and Timothy Theiss, SAE Int. J. Fuels Lubr. April 2015 8:50-61; doi: 10.4271/2015-01-0888

- “Compatibility Assessment of Plastic Infrastructure Materials with Neat Diesel and a Diesel Blend containing 20 Percent Fast Pyrolysis Bio-Oil”, Michael D Kass, Chris Janke, Raynella Connatser, Sam Lewis, James Keiser and Timothy Theiss, SAE Int. J. Fuels Lubr. April 2015 8:80-94; doi: 10.4271/2015-01-0893

- “Corrosion of Stainless Steels in the Riser During Co-Processing of Bio-Oils in a Fluid Catalytic Cracking Pilot Plant”, M.P. Brady, J.R. Keiser, D.N. Leonard, A.H. Zacher, K. J. Bryden, G.D. Weatherbee, Fuel Processing Technology, Jan 31, 2017; doi: 10.1016/j.fuproc.2017.01.041

Publications and Presentations (1)

- “Compatibility Assessment of Elastomeric Infrastructure Materials with Neat Diesel and a Diesel Blend containing 20 Percent Fast Pyrolysis Bio-Oil”, Michael D Kass, Chris Janke, Raynella Connatser, Sam Lewis, James Keiser and Timothy Theiss, SAE 2015 World Congress & Exposition, April 20-23, 2015, Detroit MI

- “Compatibility Assessment of Plastic Infrastructure Materials with Neat Diesel and a Diesel Blend containing 20 Percent Fast Pyrolysis Bio-Oil”, Michael D Kass, Chris Janke, Raynella Connatser, Sam Lewis, James Keiser and Timothy Theiss, SAE 2015 World Congress & Exposition, April 20-23, 2015, Detroit MI

- “Corrosion Issues In Biomass-Derived Oils”, James R Keiser, Michael P Brady, Samuel A Lewis, Sr, Raynella M Connatser, Michael Kass and Donovan N Leonard, EPRI International Conference on Corrosion in Power Plants, October 13-15, 2015, San Diego CA.

Publications and Presentations (2)

- “Materials Compatibility Issues With Biomass-Derived Oils”, James Keiser, Michael Brady, Michael Kass, Samuel Lewis, Sr., Raynella Connatser and Donovan Leonard, 2015 TAPPI PEERS conference, October 26-28, 2015, Atlanta GA

- “Materials Issues In Thermochemical Production, Processing and Utilization of Bio-Oil”, James R Keiser, Michael P Brady, Samuel A Lewis, Sr, Raynella M Connatser, Michael D Kass, Donovan N Leonard and Christopher J Janke, Paper 7867, NACE International Corrosion 2016 Conference & Expo, March 6-10, 2016, Vancouver, BC

- “Corrosion Issues In Production And Processing Of Bio-Oils”, James Keiser, Michael Brady, Samuel Lewis, Sr., Raynella Connatser, Rachid Taha, Donovan Leonard and Matthew Frith, presented at and published in proceedings of TAPPI PEERS Corrosion 2016 Conference held in Jacksonville, FL

Presentations (without publications)

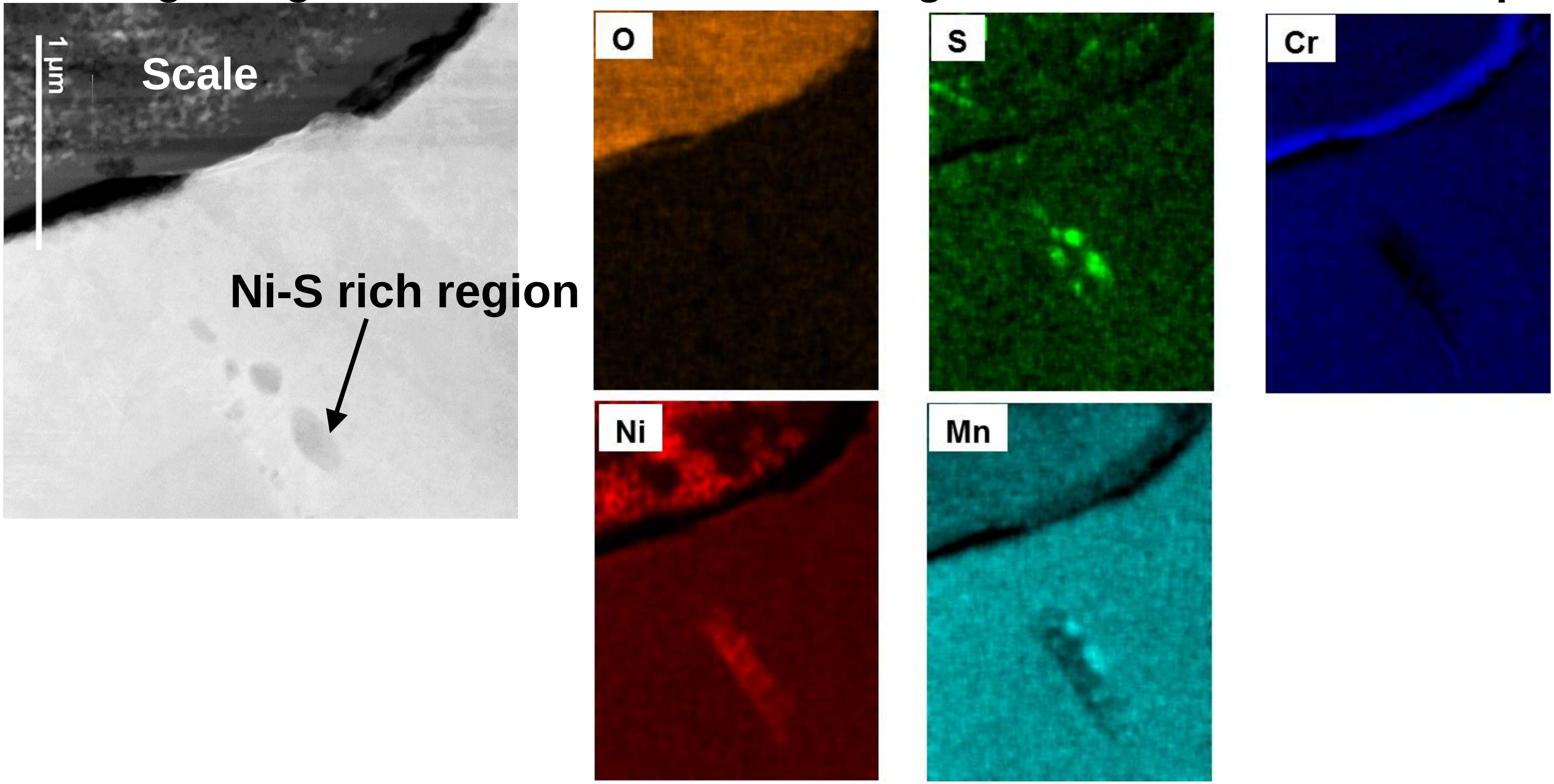
- “Effect Of Biomass-Derived Oils On Containment Materials”, James R Keiser, Michael P Brady, Samuel A Lewis, Sr, Raynella M Connatser, Michael Kass and Donovan Leonard, tcbiomass2015, Chicago, November, 2015
- Invited – “Corrosion Issues In Bio-Oil-Derived Oils”, James Keiser, Michael Brady, Samuel Lewis, Sr, Raynella Connatser and Donovan Leonard, University of Toronto Annual Research Review meeting, November, 2015
- Invited – “Materials Degradation In Biomass-Derived Oils”, Jim Keiser, Mike Brady, Sam Lewis, Maggie Connatser, Mike Kass, Donovan Leonard and Matt Frith, to Materials Technology Institute annual meeting, June 14, 2016, Knoxville, TN
- Poster Presentations at TCS2016, Chapel Hill, NC
  - “Compatibility of Fast-Pyrolysis Bio-oil with Infrastructure Elastomers”, Kass, Janke, Connatser, Lewis and Keiser
  - “Development of a Low Volume Corrosive Tendency Screening Test”, Connatser, Keiser, Lewis, Frith and Brady
  - “Corrosion Studies With Model Bio-oils”, Frith, Connatser, Lewis Keiser
  - “Compatibility Of Structural Materials With Biomass-Derived Oils”, Keiser, Brady, Lewis, Connatser, Leonard, Frith

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 Leaders – Jim Keiser, Maggie Connatser, Sam Lewis and Matt Frith
- Round Robin Study-Task Leaders – Maggie Connatser and Sam Lewis
- Test Development-Task Leaders – Matt Frith

STEM Analysis Suggests Internal S Attack Not Associated With Cr For 201 Stainless Steel

High Magnification Cross-Section Image and STEM Elemental Maps



S associated with Mn/Ni not internal Cr-sulfide (may help corrosion resistance)

Work ongoing to better understand differences with 316L and 304L: emphasis on obtaining additional/longer-term exposures of multiple alloys for study