DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Materials Degradation In Biomass-Derived Oils

March 6, 2019
Advanced Development and Optimization Review
James Keiser
Oak Ridge National Laboratory
Goals/Objectives/Expected Outcome

• Identify and/or develop materials specifically suited for use in bio-oil production, processing, storage and transporting environments

• The presence of significant quantities of oxygen-bearing compounds cause bio-oils to be corrosive to metallic and non-metallic materials

• We are using many techniques to characterize corrosive behavior:
  - Chemical characterization of bio-oil components
  - Laboratory corrosion studies of metallic and non-metallic materials
  - Field corrosion studies in operating biomass liquefaction systems
  - Examination of exposed samples and liquefaction system components
  - Fundamental study of surface interactions of bio-oil components and materials

• We expect to be able to recommend metallic and non-metallic materials that will perform sufficiently well that no liquefaction technology fails to be commercialized because of corrosion issues
## Key Milestones

<table>
<thead>
<tr>
<th>Key Milestone</th>
<th>FY 2016</th>
<th>FY 2017</th>
<th>FY 2018</th>
<th>FY 2019</th>
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<tbody>
<tr>
<td>MS 17-1 Provide spool piece for exposure</td>
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<tr>
<td>MS 17-2 Publish organic cmpd test results</td>
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<tr>
<td>MS 17-3 Publish chem analysis test results</td>
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<td>MS 17-4 Submit round robin study report</td>
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<tr>
<td>MS 18-1 Complete plastic compatibility study</td>
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<td></td>
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<tr>
<td>MS 18-2 Provide spool piece to Canmet</td>
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<tr>
<td>MS 18-3 Submit paper on leaching of Fe</td>
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<tr>
<td>MS 18-4 Complete exposure of non-metallics</td>
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<tr>
<td>MS 18-5 Submit paper on characterization study</td>
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<tr>
<td>MS 19-1 Identify leaching trends in 3 alloys</td>
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<tr>
<td>MS 19-2 Make 4 oral presentations at TCS 2018</td>
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<tr>
<td>MS 19-3 Make oral presentation at Corrosion 2019</td>
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<tr>
<td>MS 19-4 Complete evaluation of elastomer pump materials</td>
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<tr>
<td>MS 19-5 Submit paper on polymer permeation</td>
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</tbody>
</table>

**TODAY**
## Project Budget Table

<table>
<thead>
<tr>
<th>Project Tasks in FY17 and FY18</th>
<th>Project Funding (Actual)</th>
<th>Project Spending and Carryover</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total DOE Funding in FY17 &amp; FY18</td>
<td>Project Team Cost Shared Funding</td>
</tr>
<tr>
<td>Metallic corrosion studies, coordinate project</td>
<td>$555,884</td>
<td>Not defined*</td>
</tr>
<tr>
<td>Analyze exposed samples, identify and/or develop alloys</td>
<td>$478,097</td>
<td>Not defined*</td>
</tr>
<tr>
<td>Chemically characterize corrosive components of bio-oils</td>
<td>$478,109</td>
<td>Not defined*</td>
</tr>
<tr>
<td>Non-metallic corrosion studies</td>
<td>$334,470</td>
<td>Not defined*</td>
</tr>
<tr>
<td>Round robin study of analysis techniques</td>
<td>$89,536</td>
<td>Not defined*</td>
</tr>
<tr>
<td>Systematic study of effects of bio-oil components</td>
<td>$106,242</td>
<td>Not defined*</td>
</tr>
<tr>
<td>Development of corrosivity test specific to bio-oils</td>
<td>$56,271</td>
<td>Not defined*</td>
</tr>
</tbody>
</table>

*Collaborators contributed significant in-kind support by providing bio-oil samples and exposure sites for corrosion samples and spool pieces
Quad Chart Overview

Timeline
- Start date – October, 2016
- End date – September, 2020
- Percent complete – 78%

<table>
<thead>
<tr>
<th>DOE Funded</th>
<th>Total Costs Pre FY17**</th>
<th>FY 17 Costs</th>
<th>FY 18 Costs</th>
<th>Total Planned Funding (FY 19-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$6045k</td>
<td>$1158k</td>
<td>$899k</td>
<td>FY19-$1460k FY20-$????</td>
</tr>
</tbody>
</table>

Project Cost Share*

Partners provide bio-oils, sites for exposing samples and degraded components

•Partners: NREL, PNNL, CanmetENERGY, Iowa State University, Michigan State University, University of Maine, Aarhus University, Fortum, University of Toronto, FPInnovations, Georgia Tech

Barriers addressed:
- Ct-M – Current reactors not designed to handle harsh conditions inherent in converting biomass feedstock
- ADO-H – Materials compatibility, and equipment design and optimization

Objective:
Identify suitable materials for structural components of biomass liquefaction and processing systems

End of Project Goal
Structural materials will be identified that are suitable for any biomass type and processing technique so that materials issues do not prevent commercialization of any biomass liquefaction technology
1 – Project Overview

• Because of the significant oxygen content of biomass, the oils derived from biomass contain compounds corrosive to many structural materials – both metallic and nonmetallic

• By characterizing bio-oils to identify the corrosive components, using laboratory corrosion tests to determine the corrosiveness of individual bio-oils, providing samples for exposure in operating liquefaction systems, and examining exposed samples and system components we expect to determine corrosion mechanisms and identify corrosion resistant materials

• This project will provide information essential to designers and operators of current and future biomass liquefaction systems

• In order to successfully construct and operate commercial scale biomass liquefaction facilities, it is essential that structural materials be identified that have sufficient resistance to the environment so that the facilities can be operated successfully for many years
## 1 – Project Overview

<table>
<thead>
<tr>
<th>Task</th>
<th>FY2017</th>
<th>FY2018</th>
<th>FY2019</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characterize as-received bio-oil</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Conduct metallic corrosion studies</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Conduct nonmetallic degradation studies</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Provide samples &amp; pipe spoolpieces to collaborators</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Analyze exposed samples and pipe sections</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Participate in round robin study of analysis techniques</td>
<td>X</td>
<td>X</td>
<td>Moved – separate project</td>
</tr>
<tr>
<td>Develop test to determine bio-oil corrosivity</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Study corrosion effect of individual bio-oil components (EIS studies)</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Conduct fundamental study of surface interactions between metals &amp; selected bio-oil components</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Conduct neutron studies of surface behavior of nonmetallic materials in bio-oil components</td>
<td></td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>
2 – Approach (Management)

• All supported participants are staff members in ORNL’s Materials Science & Technology Division or Energy & Transportation Science Division and these staff members interact by phone, e-mail and in person on almost daily basis.

• Utilize the wealth of expertise and equipment available at ORNL.

• 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 and we communicate with these partners through phone and e-mail as well as face-to-face meetings at conferences, workshops, review meetings and on-site visits.

• Communicate results through quarterly reports, regular webinars with BETO, technical publications, conference presentations and visits to sites of interested parties.
2 – Approach (Management)

• Metal corrosion testing and deployment of samples – Keiser & Brady

• Non-metals corrosion testing – Kass

• Polymer solubility fundamentals – Kass

• Characterization of exposed metallic materials – Brady & Keiser

• Development/identification of alternate alloys – Brady & Keiser

• Chemical characterization of bio-oils – Lewis & Connatser

• Test development & basic studies – Jun, Connatser & Frith

• Round robin studies – Connatser & Lewis
2 – Approach (Technical)

- Analysis 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 operating systems, field exposures of test materials, and laboratory corrosion tests of candidate structural materials
  - Employ light and advanced electron microscopy, neutron imaging 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 enable advancement of bio-oil technologies to the commercialization stage
2 – Approach (Technical)

- Our studies have addressed degradation of materials under two significantly different environments
- Transport and storage of bio-oil is expected to occur at temperatures no higher than about 50°C
- Production and subsequent hydrotreating/refining will occur in the temperature range of 350-550°C
- The degradation mechanisms are different, and the performance of candidate structural materials is significantly different in the two environments
Technical Achievement – Laboratory Corrosion Studies

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

- 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

- Also conducting long term exposures at room temperature
Technical Achievement – Laboratory Corrosion Studies
Many Metallic Materials Exhibit Unacceptable Or Marginal Corrosion Rates at 50°C

<table>
<thead>
<tr>
<th></th>
<th>Carbon steel ($)</th>
<th>2¼ Cr-1 Mo steel ($)</th>
<th>409 stainless ($$$)</th>
<th>304L stainless ($$$)</th>
<th>316L stainless ($$$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast pyrolysis bio-oil derived from pine sawdust after 1,000 hours</td>
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<tr>
<td>Above</td>
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<tr>
<td>Immersed</td>
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<tr>
<td>Fast pyrolysis bio-oil derived from guayule after 1,000 hours</td>
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<td></td>
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<tr>
<td>Above</td>
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<tr>
<td>Immersed</td>
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<tr>
<td>Hydrothermal liquefaction bio-oil derived from algae after 500 hours</td>
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<tr>
<td>Above</td>
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<td>Immersed</td>
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</table>

= <0.1 mm/y  =>0.1 & <0.25  = >0.25 mm/y
A combination of stakeholder input and surveys were conducted to determine appropriate polymers for evaluation. This process is ongoing and new materials are added periodically.

Neutron imaging task to determine solubility fundamentals.

Specimens were exposed to bio-oils. Measured properties include volume, mass, hardness, DMA.
- Neat bio-oil
- Partially upgraded bio-oil blended with diesel to form 20% blend

Challenges included:
- Obtaining sufficient quantities of bio-oil for studies
- Polymerization of bio-oil, which complicated extraction and measurement

Success factors include identification of potential incompatibilities with polymers as well as identifying polymers suitable for use.

Technical Achievement – Laboratory Corrosion Studies
The Effect Of Bio-Oil On Non-Metallic Materials Is Also An Issue And Is Being Studied

Overhead view of chamber used to expose elastomers and plastics to bio-oil & bio-oil blends. Dozens of samples are visible on the racks between the white spacers.
Technical Achievement – Laboratory Corrosion Studies

Compatibility Of 40 Elastomers And Plastics Was Evaluated In Neat Bio-Oil And A Blend Of Partially Upgraded Bio-Oil And Diesel (Bio20)

- Evaluated infrastructure plastics (including fiberglass resins) and vapor-phase compatibility

- Results have shown areas of concern (fluorocarbons) and areas of opportunity (low-cost silicone rubbers)

- Addition of 20 vol.% partially upgraded bio-oil to diesel caused unacceptably high levels of swelling in fluorocarbons and some nitrile rubbers.

- Based on their solubility parameters, ketones and other carbonyl compounds identified as likely cause of some degradation.

- Currently, evaluating the compatibility of elastomers in closed-loop flowing system in collaboration with Canmet.

<table>
<thead>
<tr>
<th>Elastomers</th>
<th>Application</th>
<th>Plastics</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorocarbons (8 types)</td>
<td>Seals</td>
<td>HDPE (high density polyethylene)</td>
<td>Structural piping material</td>
</tr>
<tr>
<td>NBR (nitrile rubber) (6 types)</td>
<td>Seals &amp; hoses</td>
<td>Polypropylene</td>
<td>Limited use in tanks and pumps</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>Seals</td>
<td>POM (polyoxymethylene, also known as acetal) (2 types)</td>
<td>Fuel lines and tank components</td>
</tr>
<tr>
<td>Fluorosilicone</td>
<td>Seals</td>
<td>Nylon (4 types)</td>
<td>Permeation barrier and seal material</td>
</tr>
<tr>
<td>Neoprene</td>
<td>Seals</td>
<td>PVDF (polyvinylidene fluoride)</td>
<td>Fuel permeation barrier for piping</td>
</tr>
<tr>
<td>SBR (styrene butadiene rubber)</td>
<td>Fuel hose cover</td>
<td>PTFE, also known as Teflon (polytetrafluoroethylene)</td>
<td>Fuel permeation barrier for piping and seal material</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>Coatings</td>
<td>PPS (polysulfone)</td>
<td>Fuel permeation barrier for piping</td>
</tr>
<tr>
<td>NBR/cork</td>
<td>Gaskets</td>
<td>PET (polyethylene terephthalate or Mylar) (2 types)</td>
<td>Fuel permeation barrier for piping</td>
</tr>
<tr>
<td>Epichlorohydrin rubber/cork</td>
<td>Gaskets</td>
<td>PBT (polybutylene terephthalate)</td>
<td>Limited use in fuel supply systems</td>
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<tr>
<td></td>
<td></td>
<td>PTU (polylactide)</td>
<td>Fuel system coating material</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Isophthalic polyester resins (2)</td>
<td>Fiberglass tank and piping resin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Terephthalic polyester resin</td>
<td>Fiberglass tank and piping resin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Novolac vinyl ester resin</td>
<td>Fiberglass tank and piping resin</td>
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</table>
Differentiating large acids from both conventional and bifunctional carbonyls allows a more complete depiction of corrosive constituents, which speeds mechanism understanding, allowing more reliable alloy selection.

**Technical Achievement – Chemical Characterization**

**Modifying Extraction/Derivatization/MS² to Examine Carboxylic Acids**

Conventional Method: aldehyde-ketone calibration standard

Bio-oil treated with modified analysis for carboxylic acid, hydroxyaldehyde, aldehyde-ketone

- Formaldehyde
- Propionaldehyde
- Propionic acid or hydroxypropanaldehyde
- Propionaldehyde with butyric acid or hydroxybutyaldehyde

<table>
<thead>
<tr>
<th>Ion Mass</th>
<th>Mass/Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>223</td>
<td>167</td>
</tr>
<tr>
<td>237</td>
<td>167</td>
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<tr>
<td>239</td>
<td>167</td>
</tr>
<tr>
<td>267</td>
<td>167</td>
</tr>
</tbody>
</table>
Technical Achievement – Chemical Characterization
Expanded Extraction/Derivatization Developed & Published For Carboxylic Acids Based On A Common Derivatization Method

• Sample preparation & derivatization
  – Deprotonate all large acids
  – Minimize char, sugar background species
  – Create DNP-hydrazone derivatives of acids by adding enough energy (heating, time) to the system & guaranteeing proton remains with -COOH group (pH 3) to discourage the resonance stabilization that usually defeats the hydrazone formation reaction

• Separation & structural determination
  – Partially separate derivatized components with high performance liquid chromatography
  – Negative ion mode electrospray ionization & allows “soft” ionization to introduce larger, minimally volatile molecules into the mass spec intact
  – Tandem mass spectrometry (fragmentation of parent ions) allows differentiation between, for example, a carboxylic acid and its isobaric hydroxyaldehydes analog
**Technical Achievement – Chemical Characterization**

This Larger Acid-Focused Method Is Currently Being Evaluated For Utility On More “Advanced” Bio-Oils Than High Acid-Content FP Oil

The MSMS of benzoic acid (an aromatic acid), with its molecular ion peak of mass 301 amu, lacks the strong 167 amu signal indicative of aliphatic acids. Standards were created and analyzed via the exact sequence of derivatization, chromatography, and spectrometry of benzoic and several other larger acids common to bio-oils in order to validate structural identification by tandem MS.

The MSMS of bio-oil constituent of mass 239, likely acetic acid, showing the formation of ion 167, indicative of an aliphatic carboxylic acid. Other likely aliphatic carboxylic acids were found in the bio-oil, as identified by the presence of the characteristic 2° ion at 167 amu, and are listed in the chart, inset.

<table>
<thead>
<tr>
<th>1° Ion Mass</th>
<th>2° Ion Mass</th>
</tr>
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<tbody>
<tr>
<td>223</td>
<td>167</td>
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<tr>
<td>237</td>
<td>167</td>
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<td>239</td>
<td>167</td>
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<tr>
<td>267</td>
<td>167</td>
</tr>
</tbody>
</table>
Technical Achievement – Characterization Techniques

Standardization Of Analytical Characterization Techniques

• Study led by Ferrell (NREL), Olarte & Padmaperuma (PNNL) & ORNL joined as a participant, FY2015-FY2018

• Identified and evaluated 15 test methods over 4.5 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)

• ASTM method accepted: carbonyl titration (NREL lead: Christiansen/Ferrell)

• Will be separate project in FY2019
Corrosion Resistance Was Measured For A Structural Steel in Bio-Oil Constituents

- \( R_2 \) determined from electrochemical impedance spectroscopy (EIS)
- Identified corrosivity of lactobionic acid (Lowest \( R_2 \))
- \( R_2 \)-based corrosion resistance for other alloys being determined
- Current studies are measuring effects of 2 or more bio-oil constituents
- Synergy w/project chemical characterization task to understand constituent effects

16 individual bio-oil constituents tested (with 0.1 molal)
Technical Achievement – Field Exposures

Corrosion Samples And Pipe Spool Pieces Are Provided To Collaborators

Spool piece exposed in NREL pyrolysis system

Spool piece exposed in Canmet pyrolysis system

Samples exposed in freeboard of NREL pyrolysis system

Samples immersed in room temp bio-oil for long term exposure
304L SS Reactor from Iowa State Pyrolysis Process Development Unit

- Target areas for analysis to understand mechanism(s) of corrosion attack
- Full exposure history available for this example (~500 h at 500°C, primarily red oak)
- Compare with exposures of multiple alloys in other pyrolysis systems
Technical Achievement – Exam Of Exposed Components
STEM at Internal Attack in Iowa State Reactor-Alloy
Grain Boundary Shows Internal Oxide, Not Sulfide

- No sulfur enrichment at deepest internal attack region (just background noise)
  - other longer pyrolysis exposures showed sulfur was key at internal attack front

- Nanoscale Cr deplete, Ni enrich at alloy grain boundary associated w/attack
  - expands range of attack mechanisms observed in pyrolysis environments

- Compare with ongoing studies of components and test alloy exposures
  - multiple exposure times to assess kinetics (want exposures > 1000 h, hard to find)
4 – Relevance

• Our goal is to determine corrosion mechanisms and identify materials with sufficient corrosion resistance so that corrosion does not prevent commercialization of a liquefaction technology

• Recognize that corrosion in biomass-derived oils is unique and could result in premature failure of improperly chosen components of a liquefaction facility

• By identifying corrosion mechanisms and corrosion resistant materials, we will enable the bioenergy industry to successfully demonstrate their technologies and increase the likelihood of successful commercialization of their technologies

• Utilization of corrosion resistant materials could result in a reduction in construction costs and would most definitely decrease maintenance costs

• The result of our studies are being presented at conferences, in quarterly reports and in open literature publications
5 – Future Work

• We will continue to identify and characterize the corrosive components in various bio-oil samples

• We will continue studies to determine the effects on corrosivity of individual components of bio-oils

• We will continue long term exposure of metallic and nonmetallic samples in “raw” bio-oil as well as exposure of samples and spool pieces in high temperature environments in operating liquefaction systems

• Most of our milestones over the next 18 months include conference presentations/publications as well as open literature publications to disseminate the results of our studies

• We will continue with the more fundamental studies of surface interactions between bio-oil components and structural materials both metallic and nonmetallic
Summary

• Our objective is to be able to recommend corrosion resistant structural materials so that corrosion issues do not prevent successful commercialization of any biomass liquefaction technology.

• We are accomplishing this by identifying corrosive components in bio-oils, determining corrosion mechanisms, identifying corrosion resistant materials and providing guidance on the selection of suitable materials for construction of biomass liquefaction systems.

• This is of relevance to BETO because bio-oil corrosion of structural materials is recognized as a significant issue for designers of commercial biomass liquefaction systems.

• We still have things to learn about corrosion mechanisms and the performance of alternate materials in bio-oil and the environments associated with bio-oil production and subsequent treatment.
Additional Slides
Responses to Previous Reviewers’ Comments

• Questions were raised about the extent of sample types we have studied – our reply was that we have examined samples from a wide range of biomass types – red oak, pine, corn stover, switch grass, guayule and algae that were processed by fast pyrolysis, hydrothermal liquefaction and/or hydropyrolysis; availability of sufficient quantities is the primary limiting factor

• A question was asked if we could make a firm correlation between ketone/aldehyde content and degradation of elastomers – our reply was that we need to conduct more studies before drawing a firm conclusion

• A reviewer raised a concern about disconnect between pyrolysis oil characterization, low temperature corrosion studies and HTL focus of the future – our reply was characterization emphasized fast pyrolysis oil because that is primarily what has been available; low temperature corrosion tests are applicable to storage and transport of raw bio-oil; we are working with PNNL to get significant quantities of HTL bio-oil but quantities available in FY15 & FY16 have been very limited
Cross-Sections Show Internal Attack of Stainless Steels in Multiple Process Settings

- 304L, 316L, 316H stainless steels, exposure at 450-550°C for times in the 100-1000 h range
- Multiple lab, pilot, and industrial locations/reactors, process conditions
- Need to determine if this internal attack is an issue. If so, what is the mechanism?
Publications, Patents, Presentations, Awards, and Commercialization

• We have made presentations, both poster and oral, at essentially all the TCS and tcbiomass conferences over the last 10 years

• We have made presentations at many of the conferences that emphasize corrosion (NACE Corrosion), the automotive industry (SAE World Conference) as well as conferences associated with the pulp and paper industry (TAPPI PEERS)

• We have a significant number of open literature publications in journals associated with biomass and bio-oil

• Commercialization will be accomplished by making research results and recommendations available to material suppliers as well as designers and operators of biomass liquefaction systems
Recent Conference Presentations Include

- Stainless Steel Corrosion in Biomass-Derived Oil Process Environments” – tcbiomass 2017
- Corrosion Studies Evaluating Organic and Aqueous Phases From Bio-oil Processing” – tcbiomass 2017
- Compatibility of Fast-Pyrolysis Bio-oil with Infrastructure Plastic Materials” – tcbiomass 2017
- Determining Aromatic &* Aliphatic Carboxylic Acids in Biomass-Derived Oils Using 2,4-Dinitrophenylhydrazine & HPLC-Tandem MS – tcbiomass 2017
- Corrosion Behavior Of Ferrous Alloys Assessed by EIS in Simulated Bio-Oils – TCS2018
- Investigation of the Role of Chelation/Complexation in the Corrosivity of Biomass-Derived Oils – TCS 2018
- Compatibility of Infrastructure Polymers with Bio-Oils and Bio-Blendstock Fuel Candidates – TCS 2018
- Degradation of Metallic Components In Biomass-Derived Oil – TCS 2018
- Corrosion Issues in Bio-Oil Production – University of Toronto Annual Research Review
- Materials Selection For Biomass Thermochemical Liquefaction – Georgia Tech symposium on Corrosion in Pulp and Paper Mills and Biorefineries
Recent Conference Presentations Include (cont)

- Compatibility Assessment of Elastomeric Infrastructure Materials with Neat Diesel and a Diesel Blend containing 20 Percent Fast Pyrolysis Bio-Oil – SAE World Conference
- Compatibility Assessment of Plastic Infrastructure Materials with Neat Diesel and a Diesel Blend containing 20 Percent Fast Pyrolysis Bio-Oil – SAE World Conference
- Fuel Systems: Material Selection and Compatibility with Alternative Fuels – SAE International 2-day short course
Recent Open Literature Publications Include

- Research Summary: Corrosion Considerations for Thermochemical Biomass Liquefaction Process Systems in Biofuel Production – *Journal of Metals*

- Compatibility Assessment of Fuel System Infrastructure Plastics with Bio-oil and Diesel Fuel – *Energy Fuels*

- Compatibility Assessment of Fuel System Elastomers with Bio-oil and Diesel Fuel – *Energy Fuels*

- Corrosion of stainless steels in the riser during co-processing of bio-oils in a fluid catalytic cracking pilot plant – *Fuel Processing Technology*

- Determining aromatic and aliphatic carboxylic acids in biomass-derived oil samples using 2,4–dinitrophenylhydrazine and liquid chromatography-electrospray injection-mass spectrometry/mass spectrometry – *Biomass and Bioenergy*

- Degradation of Components After Exposure in a Biomass Pyrolysis System – Final manuscript submitted for *NACE Corrosion 2019 Proceedings*

- Corrosion of Ferrous Alloys by Organic Compounds in Simulated Bio-Oils – Final manuscript submitted for *NACE Corrosion 2019 Proceedings*
Determining aromatic and aliphatic carboxylic acids in biomass-derived oil samples using 2,4-dinitrophenyldrazine and liquid chromatography-electrospray injection-mass spectrometry/mass spectrometry

Samuel A. Lewis Sr., a, Raynella M. Connatser, a, Mariele V. Olarte b, James R. Keiser a

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b Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352, USA

Compatibility Assessment of Fuel System Elastomers with Bio-oil and Diesel Fuel

Michael D. Kass, a, b, † Christopher J. Janke, † Raynella M. Connatser, † Samuel A. Lewis, Sr., †

† Fuels, Engine, and Emissions Research Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, United States

Perspective

Standardization of chemical analytical techniques for pyrolysis bio-oil: history, challenges, and current status of methods

Jack R. Farrell III, National Renewable Energy Laboratory (NREL), Golden, CO, USA
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Filip Stankovski, Washington State University (WSU), Pullman, WA, USA
Dietrich Meier, Thünen Institute of Wood Research (ITB), Hamburg, Germany
Ville Paasikallio, VTT Technical Research Centre Finland Ltd (VTT), Espoo, Finland

Received December 1, 2015; revised May 4, 2016; and accepted May 12, 2016
# Project Scope Change Table

<table>
<thead>
<tr>
<th>Scope Changes</th>
<th>Date</th>
<th>Logic / Reasoning</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY17</td>
<td></td>
<td>Funding for FY17 was reduced from $1,675K in FY16 to $1,100K. Effort on two tasks was stopped and effort was reduced on some tasks</td>
</tr>
<tr>
<td>FY18</td>
<td></td>
<td>Funding was reduced to $998.6K</td>
</tr>
<tr>
<td>FY19</td>
<td></td>
<td>Funding increased to $1,460K which permitted addition of tasks involving more fundamental studies</td>
</tr>
</tbody>
</table>

- **Eliminated funding for Test Development and Systematic Study tasks**
- **Reduced travel budget and Round Robin task funding**
- **Added tasks on EIS studies, neutron studies & surface studies**
## Risk Registry Table

<table>
<thead>
<tr>
<th>Risk ID</th>
<th>Process Step</th>
<th>Risk Description</th>
<th>Severity (High/Med/Low)</th>
<th>Mitigation Response</th>
<th>Planned Action Date</th>
<th>Current Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>Availability of bio-oil samples</td>
<td>Medium</td>
<td>Contact system operators to request bio-oil</td>
<td>Continuing</td>
<td>Receiving oil from NREL</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Availability of high temperature sites to expose corrosion samples</td>
<td>Medium</td>
<td>Contact system operators to request access to exposure sites</td>
<td>Continuing</td>
<td>Gained access to sites at a few locations</td>
</tr>
<tr>
<td>3</td>
<td></td>
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