Corrosion Of Containment Materials By Pyrolysis Oils

James R Keiser, Michael A Bestor and C. Stuart Daw

Oak Ridge National Laboratory

Oak Ridge, Tennessee

There Are Many Methods To Produce Useful Products From Our Biomass Resources

- Biochemical conversion

- Thermochemical conversion

  - <u>Torrefaction</u>

    “low” temperature, solid product

  - <u>Pyrolysis</u>

    “intermediate” temperature, liquid product

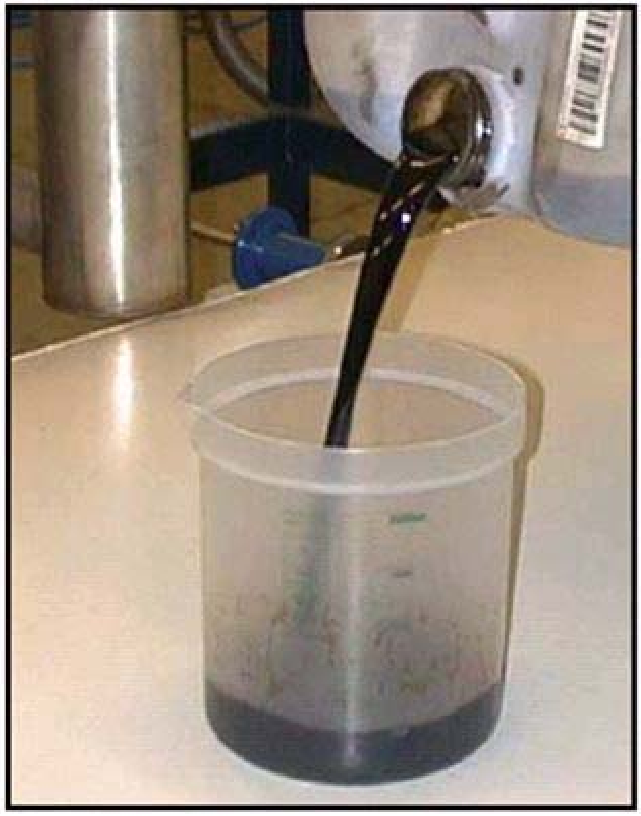
  - <u>Gasification</u>

    “high” temperature, gaseous product

Pyrolysis Oil Produced From Biomass Has Promise But Potential Problems

Pyrolysis Oils

- Are produced by elevated temperature processing of biomass
- Contain a significant amount of water and oxygen-containing compounds
- Are fairly acidic (pH of 2-3)
- Are proposed for blending with petroleum for processing in existing petroleum refineries
- Have potential to be fairly corrosive to containment vessels and pipes



Project Overview
Materials Compatibility With Pyrolysis Oil

- Since pyrolysis oil is strongly acidic, it is expected the oil would be very corrosive, so it is important to quantify the effects of pyrolysis oil (bio-oil) on structural materials used to process and contain the oil
- One proposed bio-oil processing route is to blend bio-oil with petroleum crude and process the mixture in petroleum refineries, but first the bio-oil needs to be made less corrosive
- Consequently, we need to understand the effects of pyrolysis oil on metallic materials through all the processing steps required to reduce/remove the oxygen-containing compounds in the bio-oil to make it less corrosive
- Determination of the corrosive nature of various fractions of the treated bio-oil will provide guidance on the amount of treatment required to make the bio-oil fractions suitable for processing in a petroleum refinery

Approach For The Study Of Materials Compatibility With Pyrolysis Oil

- Analysis of pyrolysis oil – To help with determination of any corrosion mechanism, a thorough analysis of the bio-oil is performed on any material used in corrosion studies

- Laboratory corrosion studies – Metallic samples of selected alloys are exposed in untreated pyrolysis oil to determine the tendency for various alloys to corrode and/or crack in bio-oil when exposed at the maximum anticipated temperature for storage and transport of bio-oil (50˚C)

- Field corrosion studies – Pipe sections and corrosion samples were provided to the National Renewable energy Laboratory (NREL), and are available to any interested party, for exposure in their pyrolysis system to assess the performance of materials when exposed in operating systems

Preparations Made For Corrosion Testing

- Test conditions were selected through discussions with staff members from other laboratories
- Four test systems were constructed for exposing samples to pyrolysis oil at 50˚C
- Samples of pyrolysis oil were requested from laboratories and companies producing pyrolysis oil

Two test systems used for pyrolysis oil corrosion tests

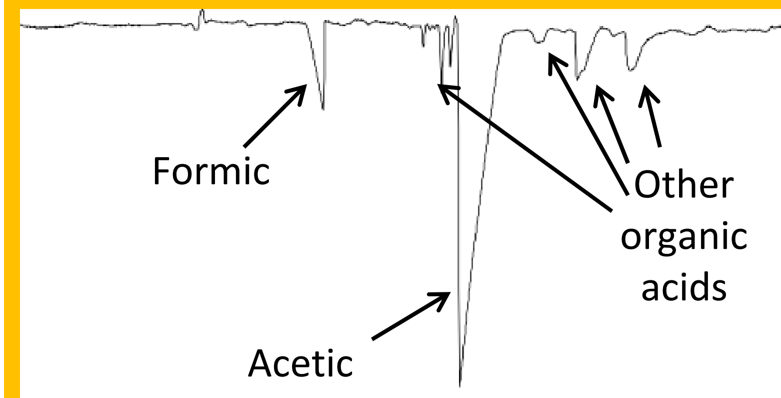
Samples used to assess localized, general and stress corrosion cracking

Pyrolysis Oil Provided By National Renewable Energy Laboratory Has Been Analyzed

- Major constituents include:

- Furfural	10.7%
- Dodecane	6.3%
- 2-methyl-phenol	4.9%
- 3-methyl 1,2-cyclopentanedione	4.9%
- 1,2 Benzenediol	4.7%
- Phenol	4.4%
- 2,6 Di-methoxy-phenol	4.1%
- 4-Methyl-phenol	3.9%
- 2 (5H)-furanone	3.8%
- 5-methyl-2-furancarboxaldehyde	3.5%
- 2,4-dimethyl-phenol	3.5%
- 2-methoxy-phenol	3.3%

Results of electropherograph analysis to identify acidic components



Acid concentrations
Formic 0.24%
Acetic 1.9%
Estimated total acid 4%

- The concentration of acidic components is cause for concern

We Are Expecting To Obtain Pyrolysis Oil From Several Additional Sources

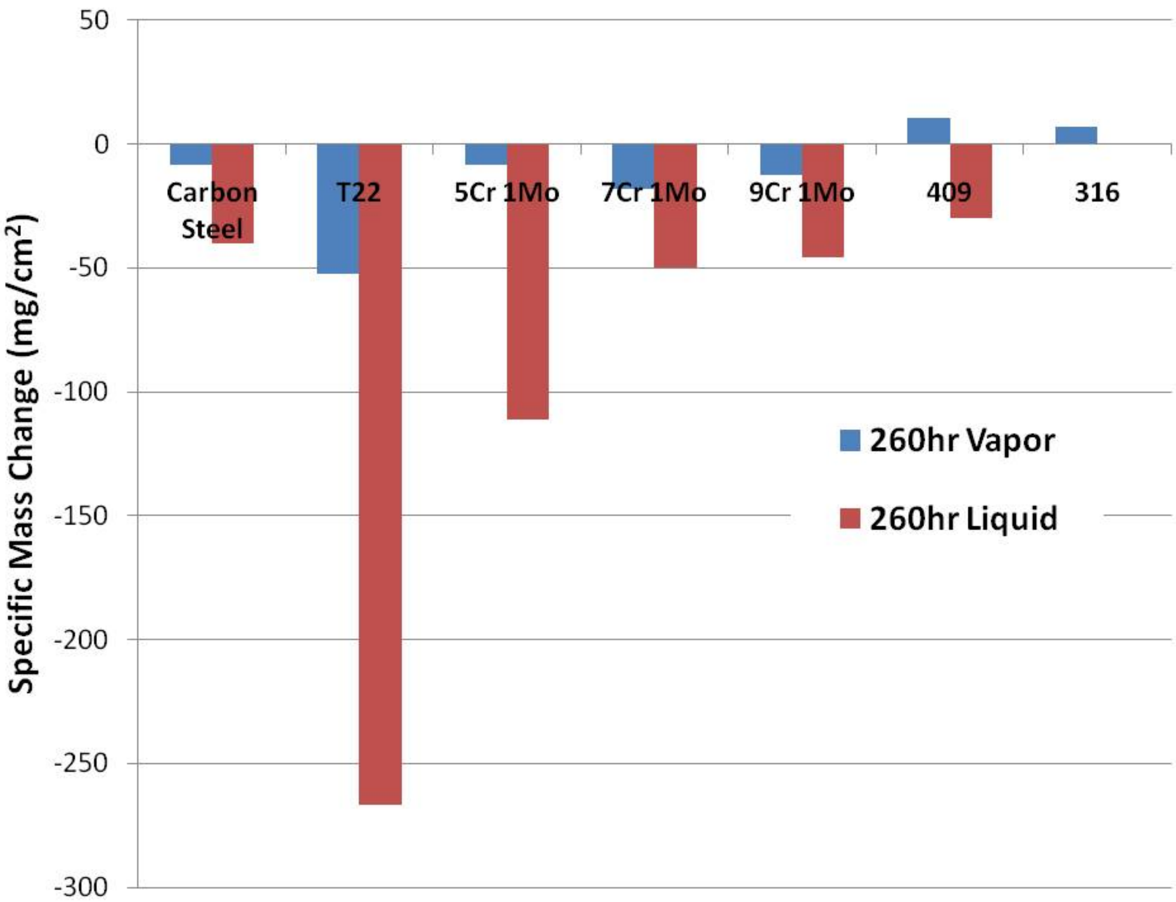
- Have been working with oil from NREL
- We're making arrangements to acquire oil for our studies from:

  - Ensyn
  - Virginia Tech
  - Iowa State University
  - U.S. Department of Agriculture
  - University of Massachusetts
  - Sandia National Laboratories
  - VTT (National research laboratory in Finland)

Corrosion Coupon Exposures Provide Information On Uniform Loss of Material

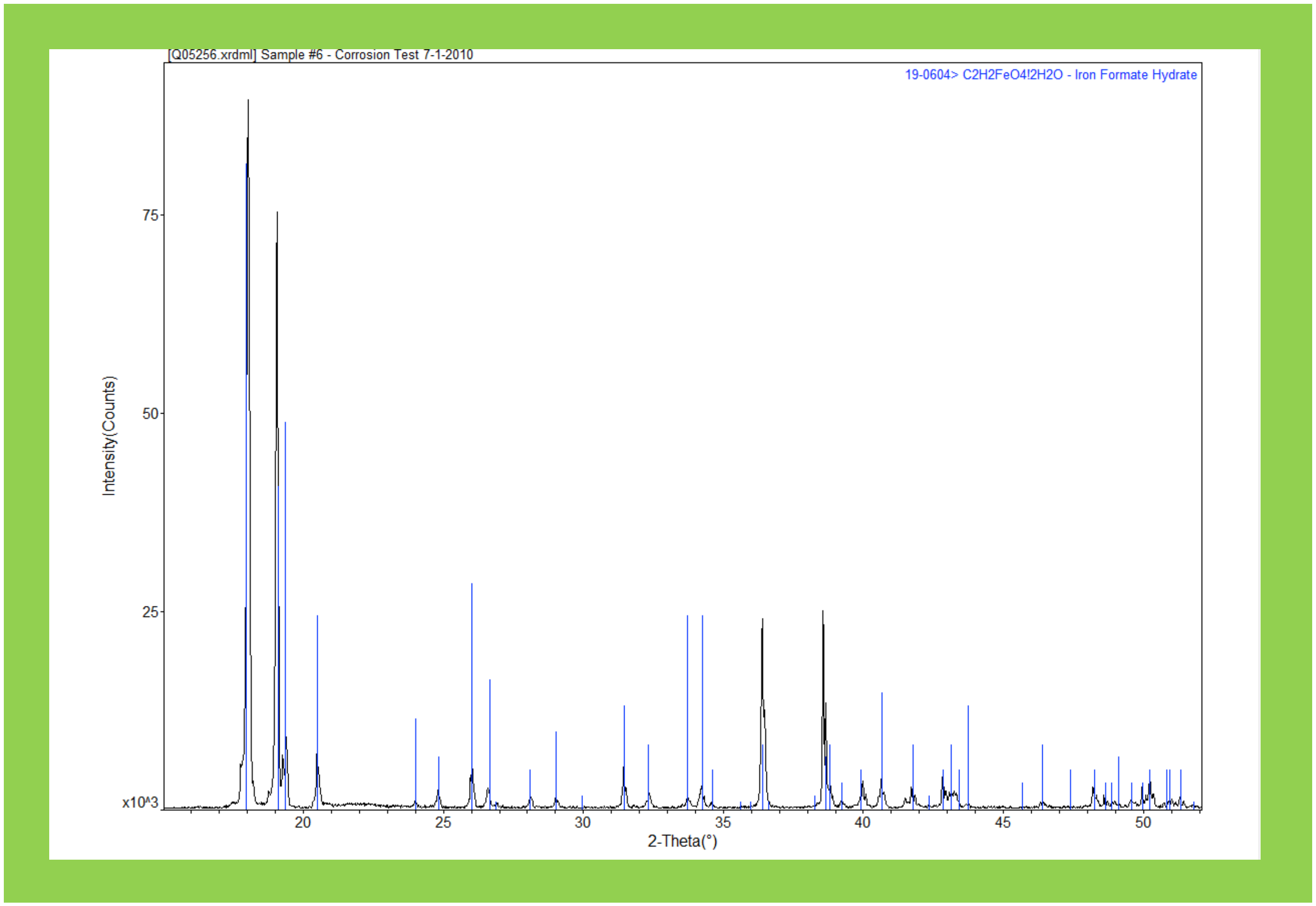
- Through discussions with NREL and PNNL it was concluded that the maximum temperature for storage and transport of pyrolysis oil would be 50°C
- Samples of typical structural materials - carbon steel and low alloy steels – were exposed in pyrolysis oil at 50°C
- Because significant corrosion rates were anticipated, a relatively short exposure period (260 hours) was used for the initial exposures
- Corrosion rates were calculated using weight loss data and assuming uniform removal of material from the surface

Weight Loss Was Generally Found To Be A Function Of Chromium Concentration



A mass change of 50 mg/cm^2 in 260 hours corresponds to a material loss rate of 2 mm/yr which is a rate far in excess of normally tolerated rates

Corrosion Product On Carbon Steel Was Identified As Iron Formate Hydrate



Iron formate hydrate would be formed by the reaction

$$Fe + 2\ HCOOH + 2\ H_2O \rightarrow H_2C_2FeO_4{\bullet}2H_2O + H_2$$

Stress Corrosion Cracking Is A Catastrophic Degradation Mechanism

- Stress corrosion cracking (SCC) can result in sudden failure of a metallic component, often with no advanced warning

- For SCC to occur, three conditions have to be met:

  - component has to be under tensile stress

  - specific corrodent has to be present

- certain operating conditions have to be met

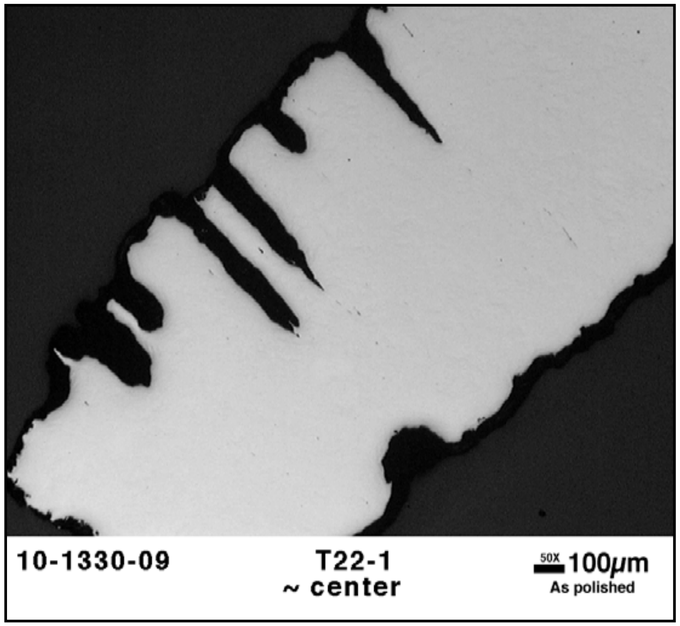
- U-bend samples are used to evaluate the propensity of a material to crack in a particular environment

Pyrolysis Oil Was Found To Cause Cracking In Carbon And Low Alloy Steels

- The potential for stress corrosion cracking was investigated by exposing U-bend samples of various materials to pyrolysis oil at 50°C
- Cracks completely through the samples were found in carbon and low alloy steels after 250 hour exposure

Cracked 2¼Cr-1 Mo sample

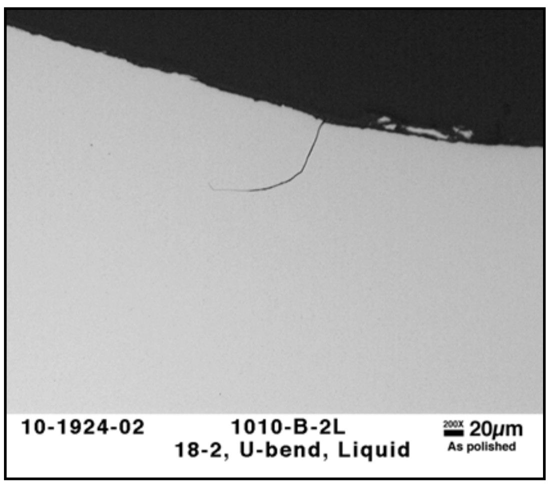
Cross-section of sample showing extensive OD cracking



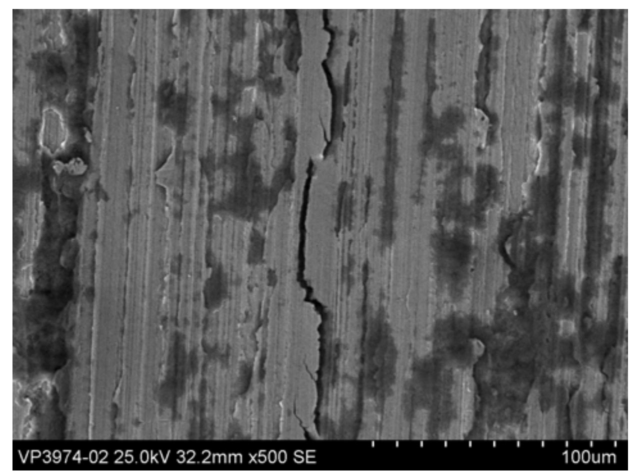
Since stainless steels showed low corrosion rates it was important to determine whether they cracked during exposure in pyrolysis oil

Crack Indications Have Been Found On Stainless Steels Exposed In Pyrolysis Oil

- Stainless steels have demonstrated low corrosion rates in pyrolysis oil at 50˚C
- Stainless steel U-bend samples have been exposed to determine if cracking will develop in stainless steels
- Crack indications were found after 500 and 750 hour exposures



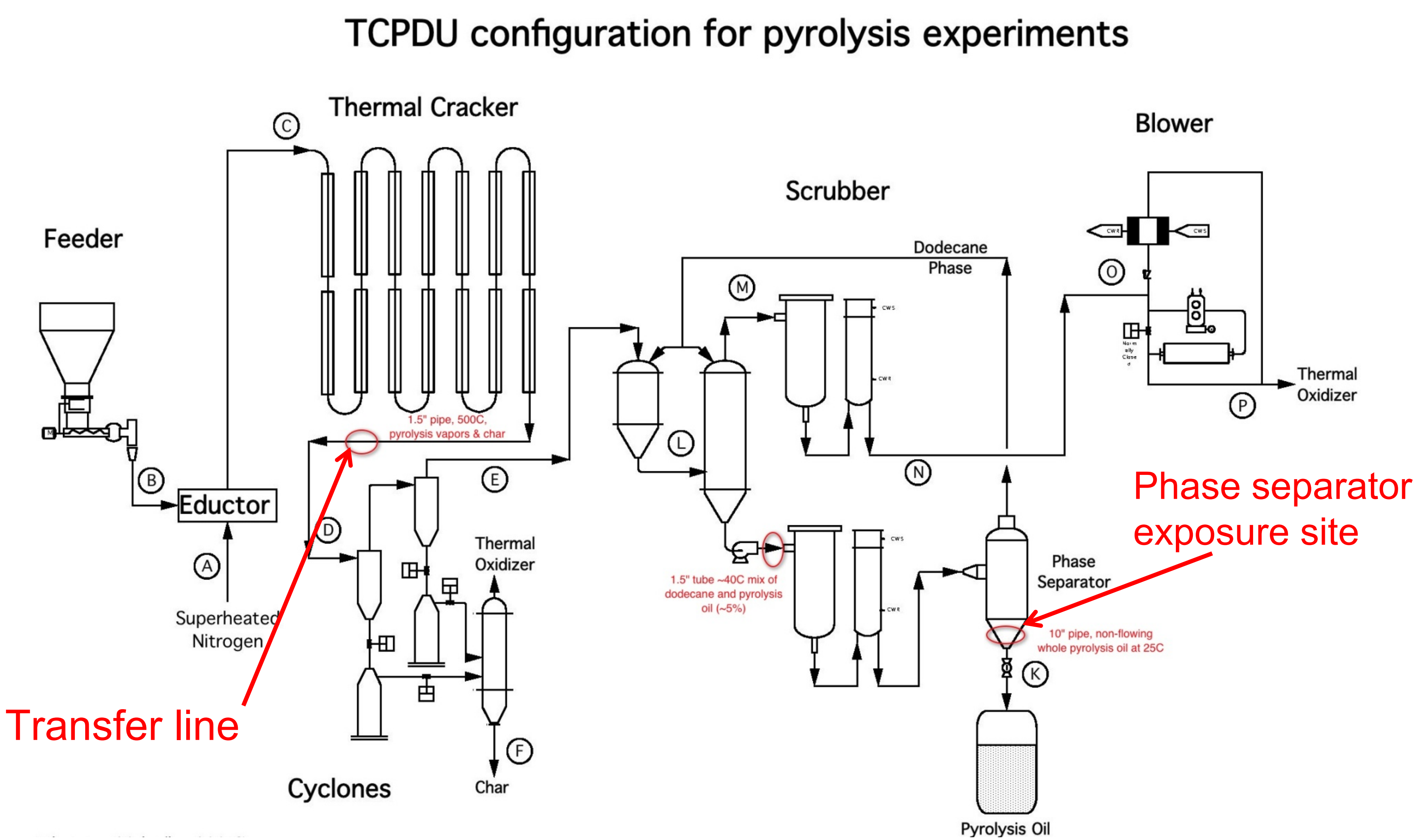
Light micrograph showing shallow crack in 18Cr-2Mo stainless steel



Scanning electron micrograph showing surface crack on stainless steel

This observation is cause for serious concern

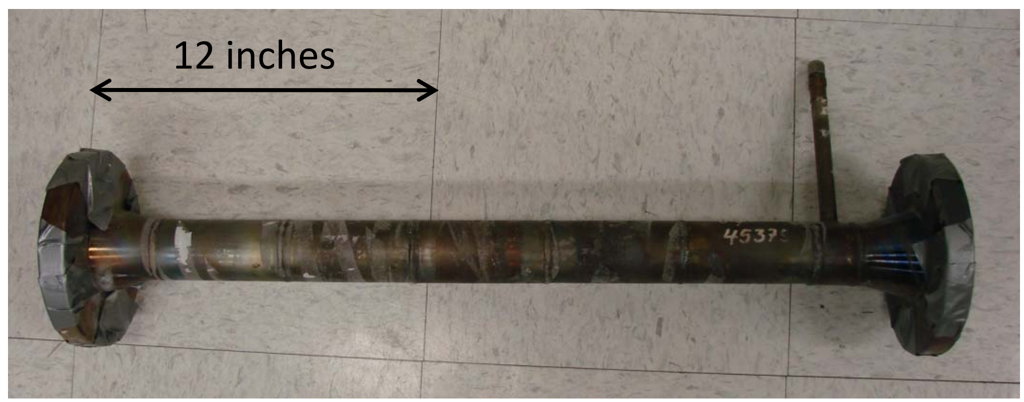
ORNL Corrosion Samples Have Been Exposed In Two Locations In The NREL Pyrolysis System



Corrosion Samples Were Exposed In An Operating Biomass Pyrolysis System

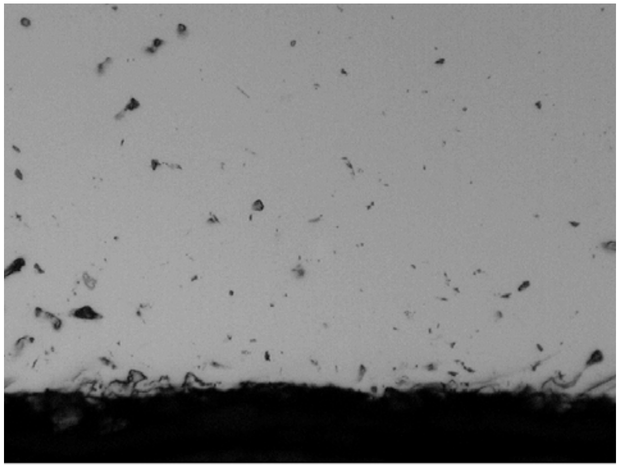
- Sections of 1½ pipe were sent to and returned from NREL after exposure as the transfer line after the thermal cracker (~550°C) in their pyrolysis system
- Sections of five different alloys were exposed
- Components are currently being examined
- Have offered to supply similar materials to other pyrolysis system operators

Material sent to NREL



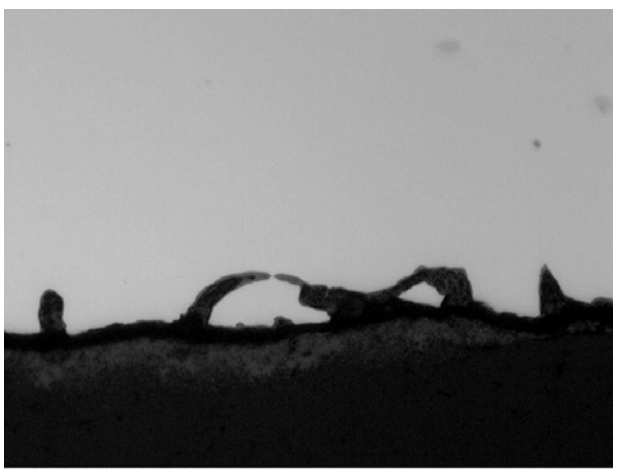
Material returned from NREL

Pipe Cross-Sections Show Evidence Of Corrosion On Internal Surfaces

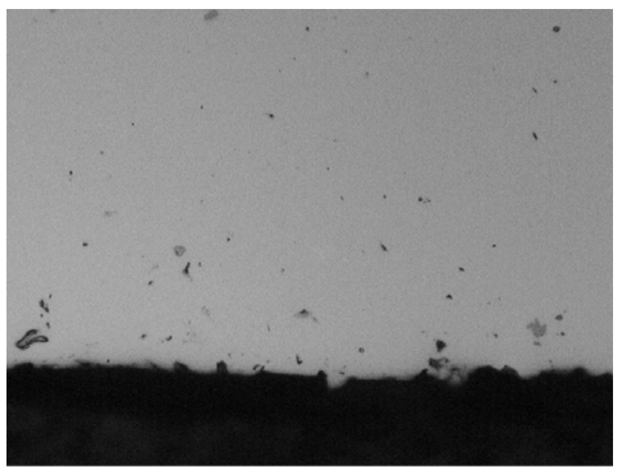


11-0015-03 310 0° I.D. 500X 10μm As polished

11-0016-04 316 0° I.D. 500X 10μm As polished



11-0017-03 347 0° I.D. 500X 10μm As polished



11-0018-04 800 0° I.D. 500X 10μm As polished

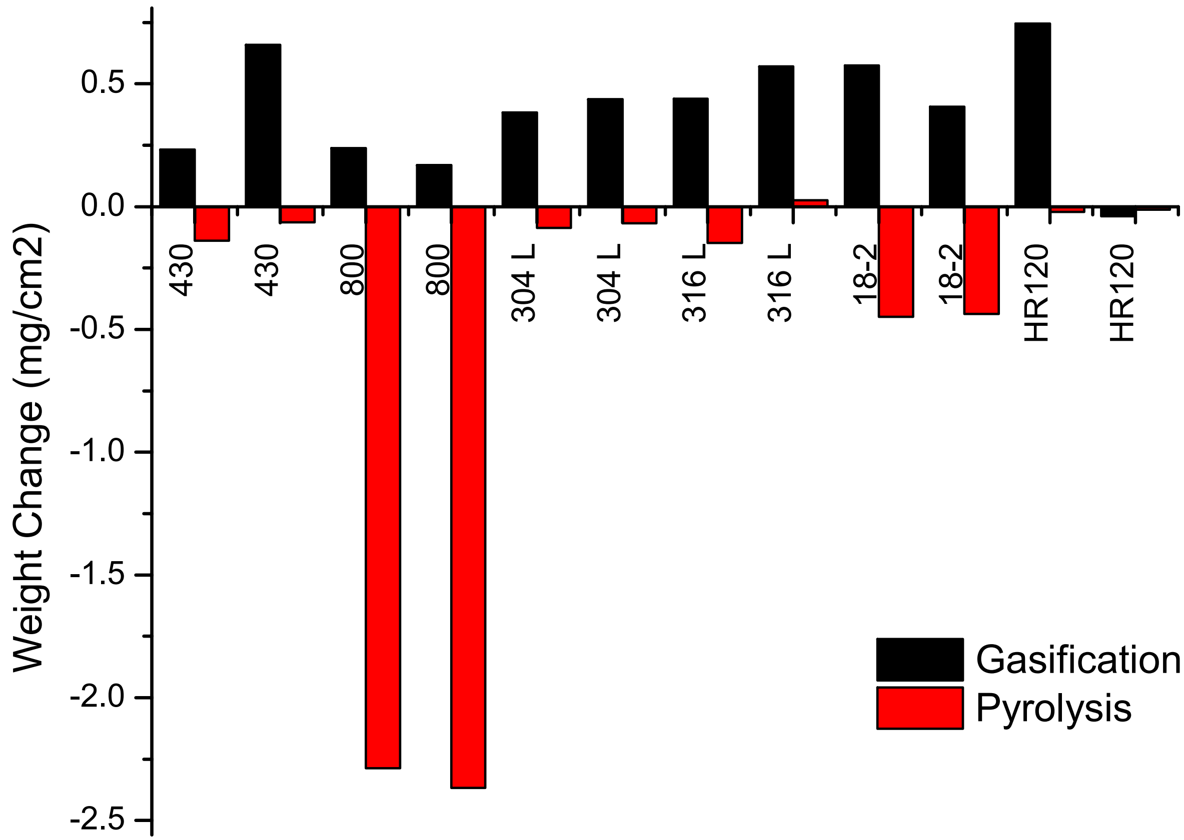
11-0019-04 825 0° I.D. 500X 10μm As polished

Corrosion Coupons Were Exposed In A Lower Temperature Environment

- Corrosion coupons were exposed by NREL in the bottom of their phase separator vessel
- One set of coupons was exposed under biomass pyrolysis conditions and one set under biomass gasification conditions
- We have weight and thickness change data

Corrosion coupons exposed in NREL phase separator vessel under pyrolysis conditions

Most Alloys Exposed To Pyrolysis Conditions Lost Weight



Compared to results from exposures at 50°C, these weight losses were relatively small

Measure Of Success

- In order for biomass-derived pyrolysis oils to be utilized, the systems used to produce, process, store and transport must have a lifetime of many years and not be subject to catastrophic failure
- This project will be successful if the operative degradation mechanism(s) of the structural materials can be identified and

  - materials can be recommended that are resistant to this/these mechanism(s), and/or

  - methods can be identified to prevent production or permit easy removal of the corrosive species

Future Work

- Modify the experimental systems to operate at much higher temperature and at elevated pressure to simulate pyrolysis oil production and hydrotreating
- Identify the bio-oil component(s) causing corrosion and cracking of structural materials
- Determine the propensity for corrosion and cracking caused by various fractions of bio-oil and bio-oil fractions that have been partially or extensively hydrotreated

Acknowledgement

- Office of Biomass Program for providing the funding for this study
- Calvin Feik of NREL for handling sample exposures in their pyrolysis system
- Adam Willoughby of ORNL for preparing samples for exposure at NREL
- NREL for providing pyrolysis oil for the current corrosion studies

Thank you for your attention

I’ll do my best to answer any questions you might have