



Corrosivity Screening of Pyrolysis Bio-Oils by Short-Term Alloy Exposures

Laboratory Analytical Procedure (LAP)

Issue Date: May 12, 2022

Dino Sulejmanovic, Jiheon Jun, James R. Keiser,
Raynella M. Connatser, and Samuel A. Lewis
Oak Ridge National Laboratory

Earl D. Christensen and Jack R. Ferrell III
National Renewable Energy Laboratory

**NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC**

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5100-82631
May 2022



Corrosivity Screening of Pyrolysis Bio-Oils by Short-Term Alloy Exposures

Laboratory Analytical Procedure (LAP)

Issue Date: May 12, 2022

Dino Sulejmanovic, Jiheon Jun, James R. Keiser,
Raynella M. Connatser, and Samuel A. Lewis
Oak Ridge National Laboratory

Earl D. Christensen and Jack R. Ferrell III
National Renewable Energy Laboratory

Suggested Citation

Sulejmanovic, Dino, Jiheon Jun, James R. Keiser, Raynella M. Connatser, Samuel A. Lewis, Earl D. Christensen, and Jack R. Ferrell III. 2022. *Corrosivity Screening of Pyrolysis Bio-Oils by Short-Term Alloy Exposures. Laboratory Analytical Procedure (LAP)*, Issue Date: May 12, 2022. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5100-82631. <https://www.nrel.gov/docs/fy22osti/82631.pdf>.

**NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC**

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5100-82631
May 2022

National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401
303-275-3000 • www.nrel.gov

NOTICE

This research was sponsored by the U.S. Department of Energy, Bioenergy Technologies Office. This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

This LAP publication work was authored, in part, by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed herein do not necessarily represent the views of the DOE or the U.S. Government.

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via www.OSTI.gov.

Cover Photos by Dennis Schroeder: (clockwise, left to right) NREL 51934, NREL 45897, NREL 42160, NREL 45891, NREL 48097, NREL 46526.

NREL prints on paper that contains recycled content.

DISCLAIMER

The *Corrosivity Screening of Pyrolysis Bio-Oils by Short-Term Alloy Exposures* analytical methods (Methods) are provided by the National Renewable Energy Laboratory (NREL), which is operated by Alliance for Sustainable Energy, LLC (Alliance) for the U.S. Department of Energy (DOE). These methods were developed and written for commercial research and educational use only.

Access to and use of these Methods shall impose the following obligations on the user. The user is granted the right, without any fee or cost, to use, copy, modify, alter, enhance, and distribute these Methods for any purpose whatsoever, except commercial sales, provided that this entire notice appears in all copies of the Methods. The user agrees to credit NREL/Alliance in any publications that result from the use of these Methods. The user also understands that NREL/Alliance is not obligated to provide the user with any support, consulting, training, or any training or assistance of any kind with regard to the use of these Methods or to provide the user with any updates, revisions, or new versions.

THESE METHODS ARE PROVIDED BY NREL/ALLIANCE "AS IS" AND ANY EXPRESS OR IMPLIED WARRANTIES, INCLUDING BUT NOT LIMITED TO, THE IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE ARE DISCLAIMED. IN NO EVENT SHALL NREL/ALLIANCE/DOE BE LIABLE FOR ANY SPECIAL, INDIRECT, OR CONSEQUENTIAL DAMAGES OR ANY DAMAGES WHATSOEVER, INCLUDING BUT NOT LIMITED TO, CLAIMS ASSOCIATED WITH THE LOSS OF DATA OR PROFITS, WHICH MAY RESULT FROM AN ACTION IN CONTRACT, NEGLIGENCE, OR OTHER TORTIOUS CLAIM THAT ARISES OUT OF OR IN CONNECTION WITH THE ACCESS, USE, OR PERFORMANCE OF THESE METHODS.

1. Introduction

- 1.1 Bio-oils are complex liquids that contain organic acids and oxygenated compounds that are corrosive to bio-oil-facing alloys during processing and storage.
- 1.2 This method allows for rapid screening of a bio-oil's corrosivity without the need for complex equipment and long-term exposures. A robust and repeatable method for assessing the corrosivity of bio-oils is necessary in order to remove materials degradation as an obstacle to research, upgrading, use, and storage of bio-oils.

2. Scope

- 2.1 The scope of this procedure involves the incubation of a representative alloy, 410 stainless steel (410 SS), specimen in bio-oil over a period of 48 hours at 50°C in a sealed container. The corrosive species in the bio-oil react with and deplete alloy elements such as iron (Fe) and/or chromium (Cr) from the specimen into the bio-oil solution. The depletion of Fe and Cr from the specimen results in a significant mass loss that can be recorded. The mass loss is directly correlated to the corrosivity of a bio-oil. Examples of bio-oils in scope include the ones produced by fast pyrolysis and catalytic fast pyrolysis, as well as liquids produced from hydrothermal liquefaction.
- 2.2 The scope of this method, in regard to alloys, is limited to one to allow for direct comparison of bio-oils. The scope does not include parameters for alloy comparison. However, this procedure can be expanded to other alloys depending on the corrosivity of the bio-oil. For example, if a bio-oil is not particularly corrosive and low mass changes are observed after incubation, alloys that are more susceptible to corrosion, such as those containing lower Cr concentration, can be used.
- 2.3 The procedure described in Section 9 should be repeated in triplicate for reliability and statistics.

3. Terminology

- 3.1 *Bio-oil* – The crude liquid product of converting solid biomass into a liquid via fast pyrolysis or other thermochemical conversion process.
- 3.2 *Pyrolysis* – Chemical decomposition of organic materials by heating in the absence of oxygen.
- 3.3 *Fast pyrolysis* – Pyrolysis conducted with rapid heating and short residence time; typically less than 10 seconds.
- 3.4 *Catalytic fast pyrolysis* – Fast pyrolysis conducted in the presence of a catalyst designed to perform partial deoxygenation.

4. Significance and Use

- 4.1 This procedure is used to determine the amount of specimen mass change in a prescribed representative alloy, 410 SS, after incubation with a bio-oil at 50°C for 48 hours. Comparison of mass changes among specimens will indicate the differences in aggressiveness of the bio-oils toward 410 SS. The more specimen mass loss is observed, the more aggressive and potentially corrosive that bio-oil is deemed among a group of bio-oil samples. This method is quantitative for relative comparison of corrosivity of various bio-oils toward 410 SS. However, this method is not quantitative for corrosion rate determination and can only be used as a qualitative comparison of corrosion rates.

5. Interferences

- 5.1 Samples of bio-oils that have been treated with external mineral acid or caustics/base after being processed will suffer interference from said externally added aggressive reagents.

6. Apparatus

- 6.1 Analytical balance capable of reading out to 0.0001 g.
- 6.2 Laboratory oven, $\pm 2^\circ\text{C}$ controllable at 50°C for 48 hours (it is important that the oven temperature be calibrated and is monitored with a secondary thermocouple).
- 6.3 Chemical fume hood.

7. Reagents and Materials

- 7.1 Reagents
 - 7.1.1 Methanol, high-performance liquid chromatography (HPLC) grade or better.
 - 7.1.2 Bio-oil samples for testing.
- 7.2 Materials
 - 7.2.1 40-mL borosilicate glass vials, disposable with a plastic screw-cap.
 - 7.2.2 Teflon wire for hanging 410 SS specimens.
 - 7.2.3 Stainless steel specimens (within 0.015% composition of that below) with a drilled hole and total surface area of $5.0\text{ cm}^2 \pm 0.3\text{ cm}^2$, polished to 600-grit SiC paper:

Table 1. Analyzed composition of 410 SS material by ICP-OES and combustion techniques (balance Fe) in weight percent (wt %). Alloying additions and metallic impurities were rounded to the nearest 0.01 wt % (impurity metals present at ≤ 0.01 wt % are not reported). Levels of O, N, and S are reported in weight parts per million.

	Cr	Cu	Mn	Mo	Ni	P	Si	V	Co	C	O	N	S
410 SS	13.10	0.05	0.46	0.02	0.20	0.02	0.31	0.04	0.01	0.04	69	630	10

7.2.4 Tweezers, at least 6" long, of at least surgical steel or better.

7.2.5 600-grit polishing paper.

7.2.6 Disposable plastic pipettes (1–3 mL).

7.2.7 One 32-oz screw-cap sealable jar/Mason jar.

8. Environmental Safety and Health Considerations and Hazards

8.1 Solvents and bio-oils should only be handled in fume hoods with proper personal protective equipment (PPE).

8.2 Hot samples and rinsates should be handled carefully.

8.3 Follow all applicable chemical handling procedures.

9. Sample Preparation and Procedure

9.1 Hand-polish all sides of three different 410 SS specimens with 600-grit paper under water until the surface is visibly shiny/metallic (note: Step 9.1 is only necessary if the specimens show visible stains or unpolished surfaces).

9.2 Rinse the polished 410 SS specimens with deionized (DI) water and methanol and allow to dry completely. Handle rinsed specimens with nitrile gloves to avoid staining the specimens.

9.3 Once dried, weigh the 410 SS specimens to four decimal places (0.0001-g) accuracy or better. Record the mass as M_{initial} .

9.4 After weighing, thread the Teflon wire through the hole in the specimen. The wire should be long enough to hold the specimen suspended just above the bottom of the vial. To hang the Teflon wire, the top of the wire should either be taped to the inside of the plastic cap or threaded through the rubber seal of the plastic cap. Once the specimen is hanging on a Teflon wire attached to the plastic cap, the cap + Teflon wire + specimen can be set aside and the addition of bio-oil to the 40-mL vial can proceed. For a visual of the sample mounting, see Figure A-1 in the Appendix.

9.5 Ensure the bio-oil is thoroughly mixed before taking an aliquot for the corrosivity study. In the case of viscous bio-oils, it is helpful to heat the bio-oil to about 30°C–40°C temperature before weighing. Homogenize the bio-oil by vortexing or shaking the

original container. Transfer the bio-oil using the disposable plastic pipettes. Weigh 25.0 g \pm 1.0 g of bio-oil by first taring the 40-mL glass vial. Record the final mass of the bio-oil to 0.0001-g accuracy.

- 9.6 Once both the specimen and the bio-oil are weighed, the specimen can now be immersed into the bio-oil by closing the cap with the specimen suspended. Ensure that the specimen is suspended just above the bottom of the vial.
- 9.7 Immediately after adding the 410 SS specimen to the bio-oil, the closed vial should be placed inside a temperature-controlled oven at 50°C \pm 2°C. The incubation should last exactly 48 hours. The vials should be placed in a secondary container such as sealable 32-oz jars.
- 9.8 Upon completion of incubation, the vials are taken out of the oven and allowed to cool for 30 minutes inside a fume hood.
- 9.9 After cooling, the cap is loosened and the specimen is taken out of the bio-oil.
- 9.10 The specimen is then immersed in 10 mL of methanol for 10 minutes.
- 9.11 The specimen is removed from the methanol soaking solution, Teflon wire is removed, and the specimen is held by tweezers, rinsed with more methanol using a squirt bottle.
- 9.12 After thorough cleaning of the specimen surface, the specimen is allowed to dry for about 10 minutes.
- 9.13 The specimen is then weighed and its mass is recorded as M_{final} .
- 9.14 Steps 9.1 through 9.13 are repeated in triplicates for the particular bio-oil.

10. Calculations

- 10.1 Determine the total surface area (SA) of the 410 SS specimens. For a disc geometry:

$$SA = 2\pi rh + 2\pi r^2,$$

where r is the radius of the disc and h is the height or thickness.

- 10.2 Determine the specific mass change (SMC), reported in milligrams per square centimeter:

$$SMC = \frac{(M_{\text{final}} - M_{\text{initial}})}{SA}.$$

- 10.3 Determine the mass change percent (MCP), reported as a percent:

$$MCP = \frac{(M_{\text{final}} - M_{\text{initial}})}{M_{\text{initial}}} \times 100.$$

11. Report Format

- 11.1 Simple table or bar chart reporting is recommended, with specific mass change units of “milligrams per square centimeter.”

12. Precision and Bias

- 12.1 Precision of the method is governed by the temperature control and length of incubation.
- 12.2 A high-corrosivity bio-oil can result in large mass change values (that exceed $-1 \text{ mg}\cdot\text{cm}^{-2}$ in SMC or -0.8% in MCP). For example, 410 SS showed $-5 \text{ mg}\cdot\text{cm}^{-2}$ or more negative mass change in a high-ash and high-moisture (HAHM) biomass pyrolysis oil.
- 12.3 If a bio-oil is not corrosive to a metallic alloy, small mass changes (-0.1 to $0.1 \text{ mg}\cdot\text{cm}^{-2}$ in SMC or -0.04% to 0.04% in MCP) can be expected. For example, 430 stainless steel ($\sim 17 \text{ wt } \% \text{ Cr}$) showed a mass change of $-0.051 \text{ mg}\cdot\text{cm}^{-2}$ or less in the aforementioned HAHM biomass pyrolysis oil.

13. Quality Control

- 13.1 *Reported significant figures:* Report masses to the nearest tenth of a milligram.
- 13.2 *Replicates:* It is recommended that triplicates be measured for each bio-oil.

14. References

[1] Raynella M. Connatser, Matthew G. Frith, Jiheon Jun, Samuel A. Lewis Sr., Michael P. Brady, and James R. Keiser. 2020. “Approaches to investigate the role of chelation in the corrosivity of biomass-derived oils.” *Biomass and Bioenergy* 133: 105446. <https://doi.org/10.1016/j.biombioe.2019.105446>.

[2] Earl D. Christensen, Steve Deutch, Cheyenne Paeper, and Jack R. Ferrell III. 2022. *Elemental Analysis of Bio-Oils by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5100-82586.

15. Appendix

- 15.1 Figure A-1 displays the alloy specimens, bio-oil, and vials (40-mL size) used for incubation with 410 SS alloy. Masses of both alloy and the bio-oil sample must be recorded.

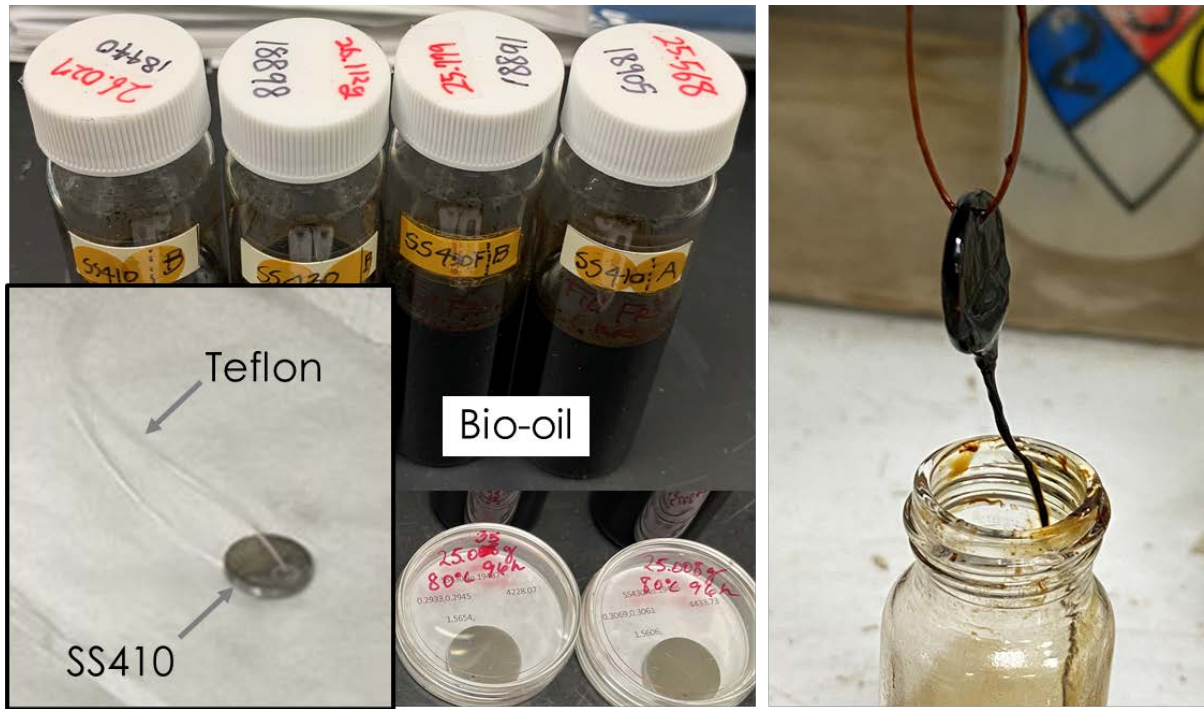


Figure A-1. Alloy specimens, bio-oil, and 40-mL vials used for incubation with 410 SS alloy