IOWA STATE UNIVERSITY
OF SCIENCE AND TECHNOLOGY

Center for Sustainable Environmental Technologies

Evaluation of Bio-oil Corrosion Characteristics

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Introduction

Petroleum crude oils contain naphthenic acids that are one of the main causes of corrosion in the petroleum industry during storage, transport, and refining. Naphthenic Acid Corrosion (NAC) has been related to three parameters: Total Acid number (TAN), temperature, and flow rate [1, 2, 3, 4]. Bio-oils do not contain naphthenic acids but do however contain other organic acids such as acetic, formic, glycolic and propanoic acid that may have similar consequences to metal surfaces. A comprehensive corrosion study needs to be completed to determine the actual effects of the organic acids in bio-oil on select metal surfaces. As a result of this study, acid number and corrosion potential of pyrolysis bio-oils can be correlated and ranked to produce a fraction that is compatible with petroleum refining equipment.

The proposed project will evaluate and compare corrosion and acid number (AN) on fast pyrolysis bio-oil produced at Iowa State University (ISU). The corrosion characteristics are evaluated using a vacuum distillation apparatus that simulates a distillation tower in a petroleum refinery. Selected metal specimens are subjected to both the liquid and vapor phase of the bio-oil. Method D664 "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration" was used to determine acidity of the bio-oil samples. Ion Chromatography (IC) is used to quantify organic acid concentration. The corrosiveness is ranked gravimetrically according to mass loss during the study. Selected metal specimens are examined by Scanning Electron Microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS) to determine morphological and composition changes on the metal surfaces.

Objectives

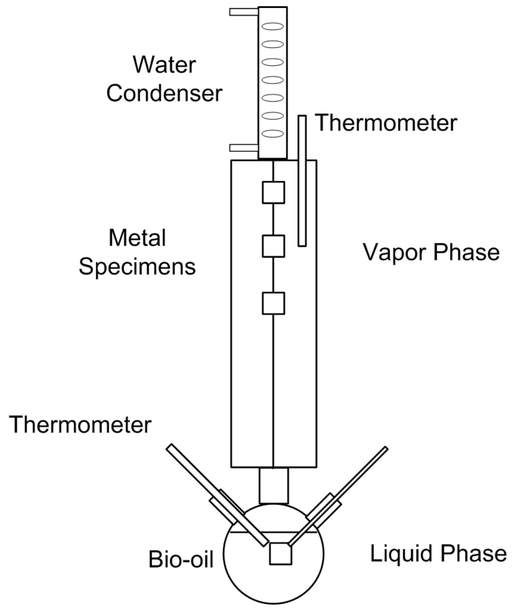
- Determine if existing petroleum refinery infrastructure can handle bio-oil as a "drop in" crude oil alternative.
- Determine if the acidic components in bio-oil cause corrosion issues with specific types of metals found in the petroleum industry.
- Evaluate metal specimens and acid composition of the bio-oil produced at ISU using a lab scale distillation tower apparatus [5].
- Determine whether acid number is a good predictor of corrosion potential.

Materials and Methods

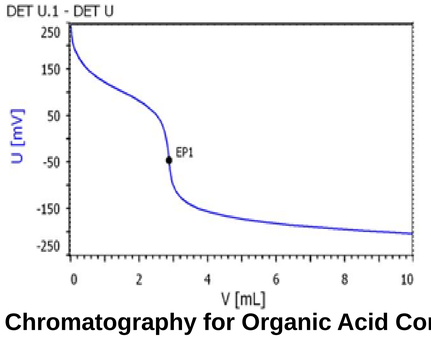
I. Modified ASTM D664—"Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration"—to determine modified acid number (MAN) of bio-oil.
II. Ion Chromatography (IC)—used to determine organic acid composition and concentration of bio-oil.
III. Tested metals 304, 316, and 17-4 in lab scale distillation tower (750mL of bio-oil at 110°C).
IV. Gravimetrically analyzed metal specimens.
V. Scanning Electron Microscopy (SEM)—used to determine if the acidic composition of bio-oils is a good representation of potential corrosion.

Experimental

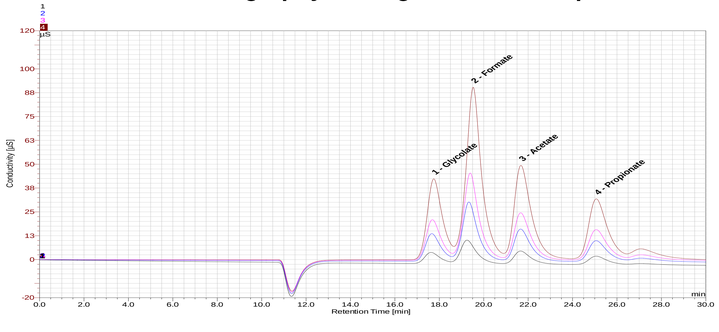
Lab Scale Distillation Tower for Evaluating Bio-oil Corrosion Characteristics



Modified ASTM Titration for Modified Acid Number



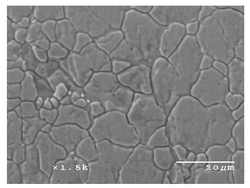
Ion Chromatography for Organic Acid Composition



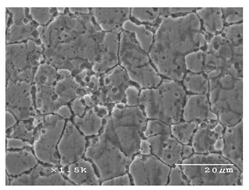
Results

Scanning Electron Microscopy – 1500X

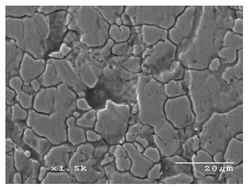
304SS Control



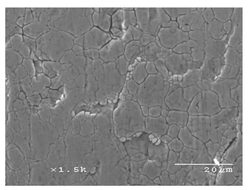
304SS Vapor Phase (top)



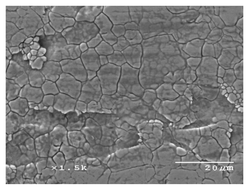
304SS Liquid Phase



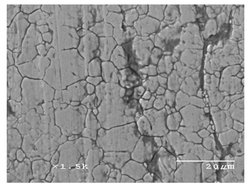
316SS Control



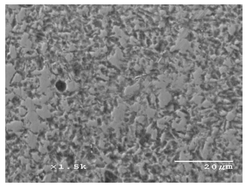
316SS Vapor Phase (top)



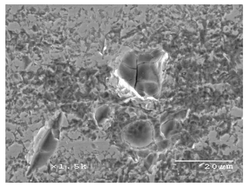
316SS Liquid Phase



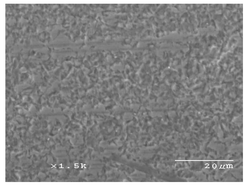
17-4 Control



17-4 Vapor Phase (top)



17-4 Liquid Phase



Conclusions

- Bio-oil presents potential corrosion issue with both 316 and 304 stainless steel metals.
- Precipitate-hardened metals such as 17-4 are little affected.
- MAN appears to be a good indicator of corrosion potential for bio-oils.
- These results do not take into account the overall type and corrosiveness of acids present.

Future Work

- Longer duration tests.
- Different types of metals.
- Energy-dispersive x-ray spectroscopy (EDS).
- Determine morphological and compositional changes on the metal surfaces.

References

1. A. Jayaraman, H. Singh, and Y. Lefebvre, Rev. Inst. Fr.Pet.**41**, 265 (1986).
2. C. M. Cooper, Hydrocarbon Process.**51**, 75 (1972).
3. E. Babaian-Kibala, H. L. Craig, G. L. Rusk, et al., Mater.Perform. **32**, 50 (1993).
4. E.B. Zeinalov, V.M Abbasov, and L.I. Alieva, Petro. Chem.**49**, 185 (2009).
5. H. D. Dettman, N. Li, J. Lou, Refinery Corrosion. CanmetEnergy-Nat. Res. Canada (2009).

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https://www.cset.iastate.edu/tcbiomass2013/

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