OAK RIDGE National Laboratory

Selection Of Materials For Storage And Transport Of Bio-Oils

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Oak Ridge National Laboratory

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U.S. DEPARTMENT OF ENERGY

In Thermochemical Liquefaction Of Biomass, There Are Two Problems to Be Addressed

- During the liquefaction process, the containment materials are subjected to conditions that sometimes cause thick scale formation and intergranular attack of 300 series stainless steels
- The as-produced bio-oils are very corrosive to materials that are typically used for transport and storage of liquid fuels at relatively low temperatures (<50°C)

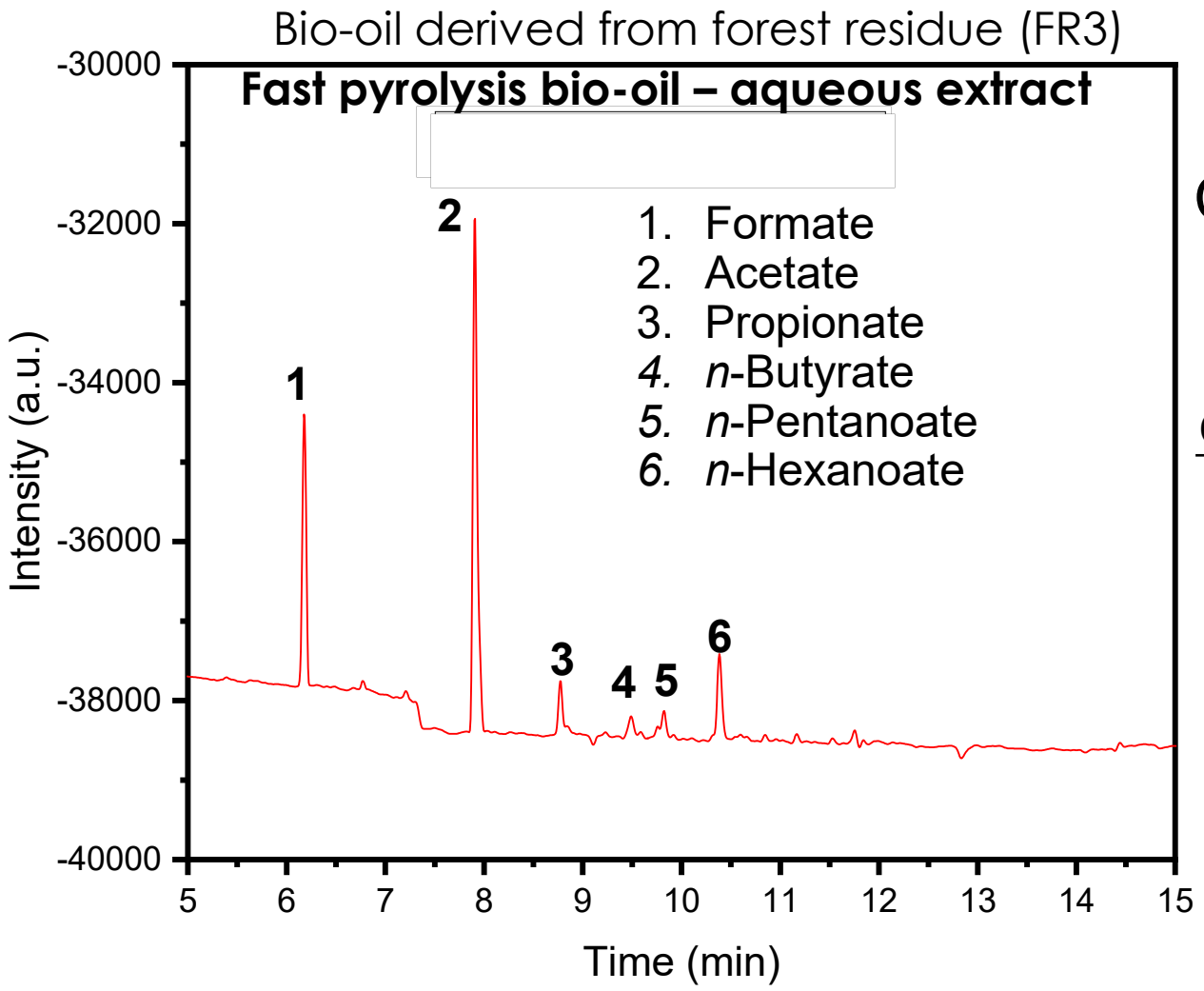
For This Presentation, We Will Address Corrosion Issues With The Storage And Transport Of Bio-Oils (Temperature ≤50°C)

Alloys With A Range Of Chromium Contents Have Been Studied

		Nominal Composition in wt %				
Alloy	Fe	Ni	**Cr**	Mo	Mn	C
1018 CS	Bal				1.0	0.13
2¼ Cr-1 Mo	Bal		**2.25**	1.0	0.4	0.1
7 Cr-1 Mo	Bal		**7.0**	1.0		
9 Cr-1 Mo	Bal		**9.0**	1.0		
409 SS	Bal		**11.0**		0.3	0.015
304L SS	Bal	9.0	**18.3**		1.7	0.02
316L SS	Bal	10.2	**16.4**	2.1	1.6	0.02

These alloys were selected with the goal of assessing the effect of chromium content on resistance to corrosion

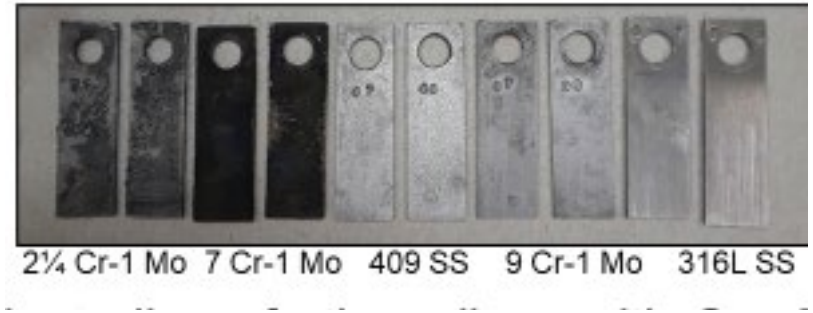
Formic and Acetic Acids are Present in Fast-Pyrolysis Bio-Oils in Significant Quantities

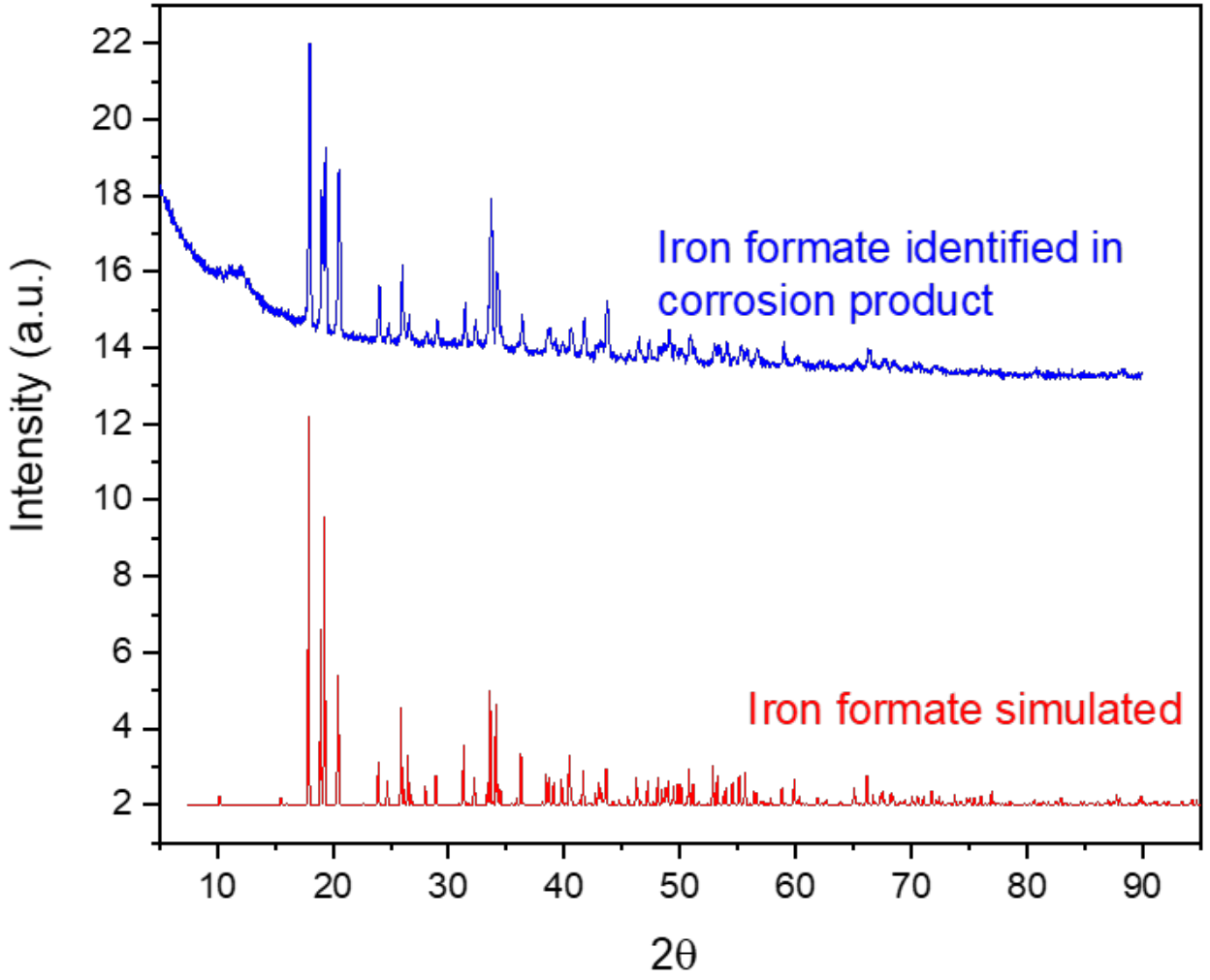


Concentration of formic and acetic acids in bio-oil:

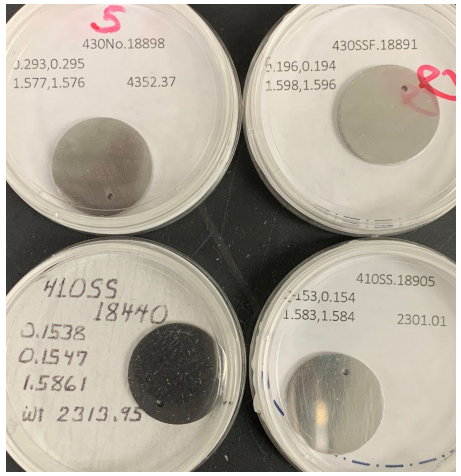
Carboxylate	R.T. (min)	Area	Concentration (µg/g bio-oil)
formate	6.18	4.303	**6491**
acetate	7.91	9.641	**19939**

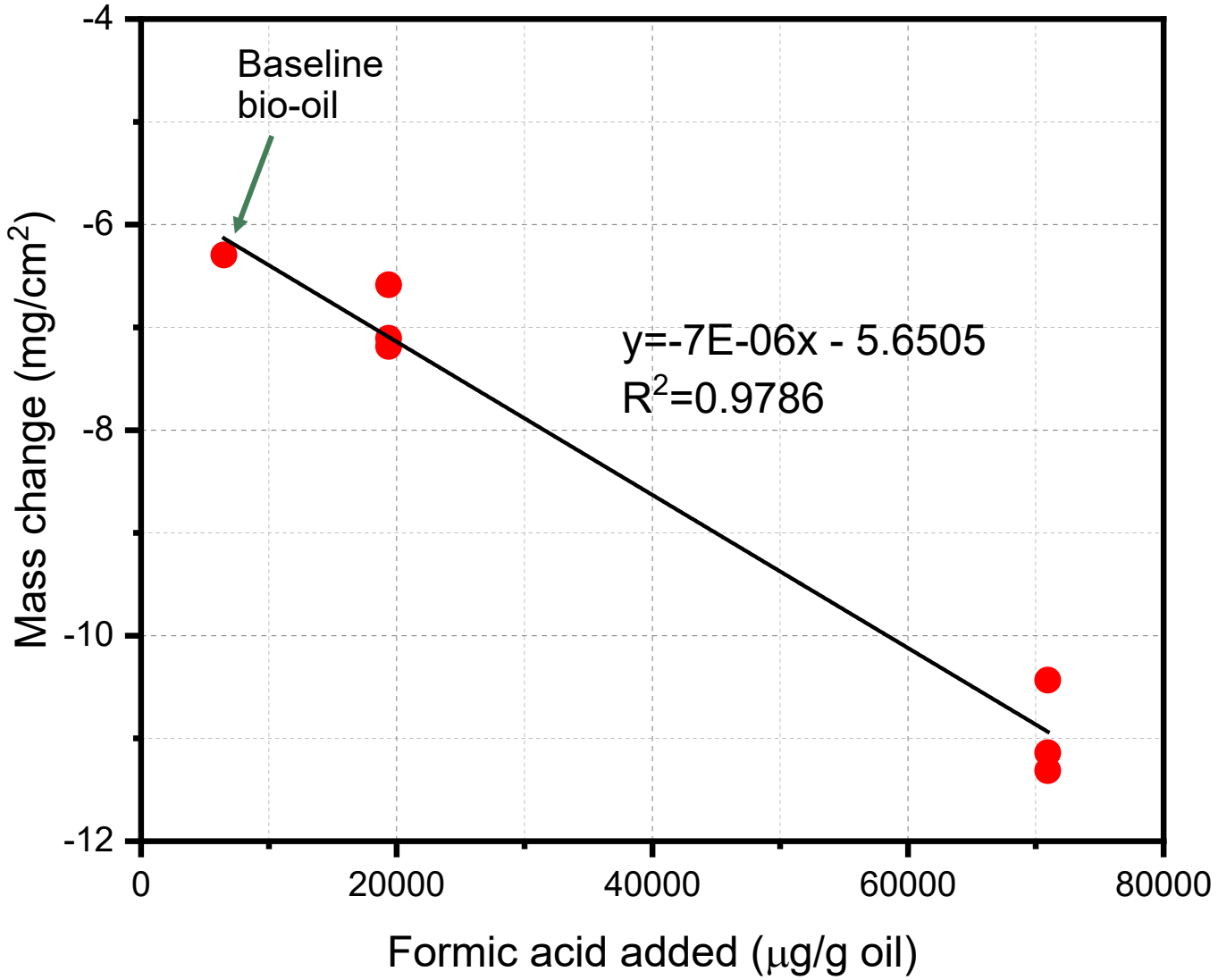
Short-term Exposures of Low-Cr Steels in Fast-pyrolysis Bio-oils revealed Iron formate as the main corrosion product





Increasing Formic Acid Resulted in Larger Mass Loss of 410 Steel at 50°C, 48 hour Exposures





Samples Have Been Exposed In Bio-Oil Under Various Conditions As Well As Diesel Fuel Reference

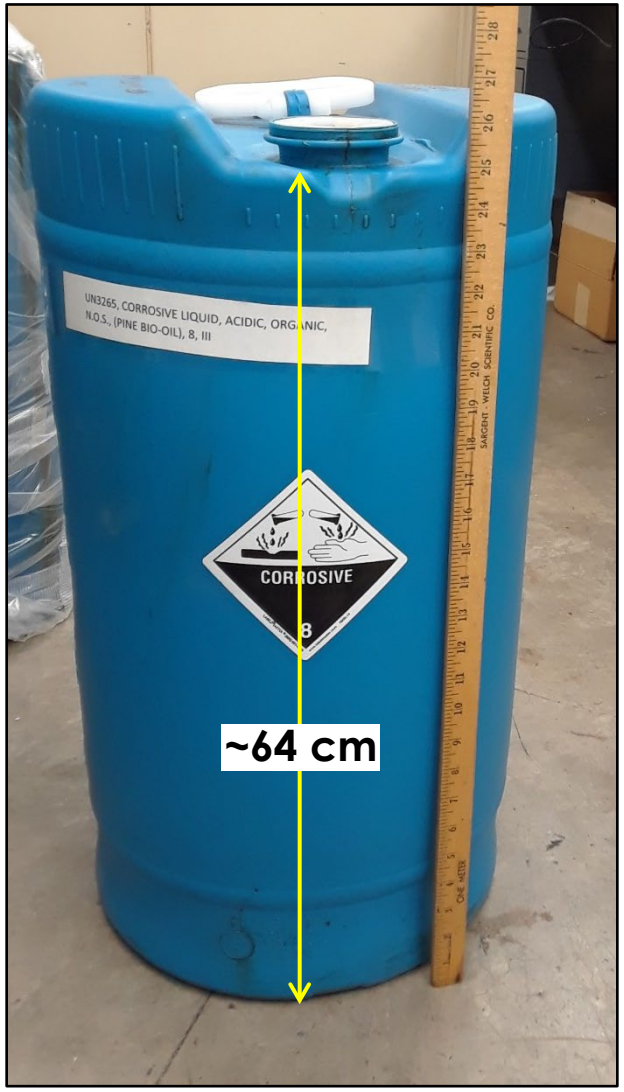
Condition	Sample Materials	Exposure Location	Fluid	Exposure Time (h)	Exposure Temperature
Partial immersion	**2¼ Cr-1 Mo, 409 SS, 316L SS**	**NREL**	**Fast pyrolysis bio-oil**	**26,743**	**~10°C**
Partial immersion	**2¼ Cr-1 Mo, 409 SS, 316L SS**	**NREL**	**Fast pyrolysis bio-oil**	**26,743**	**Room temp**
Full immersion	2¼ Cr-1 Mo, 7 Cr-1 Mo, 9 Cr-1 Mo, 409 SS, 316L SS	ORNL	Three fast pyrolysis bio-oils	12,480 & 7,650	Room temp
Full immersion	2¼ Cr-1 Mo, 7 Cr-1 Mo, 9 Cr-1 Mo, 409 SS, 316L SS	ORNL	Diesel fuel	7,650	Room temp

Two Racks Of Samples Were Prepared For Long-Term Exposure At NREL

Two 16” (40.6 cm) long samples each of three different alloys were on each rack which were inserted into two separate drums. One drum was kept in their cooled storage room (~10°C) while the other was held at room temperature.

Drum Storage Conditions At NREL

- Samples were exposed at NREL in two drums like shown in the picture
- One drum was stored in a room they attempted to maintain at about 10°C
- The other drum was stored at room temperature
- Drums were about half full of bio-oil
- Samples were exposed in drums for 26,743 h (~3 y)



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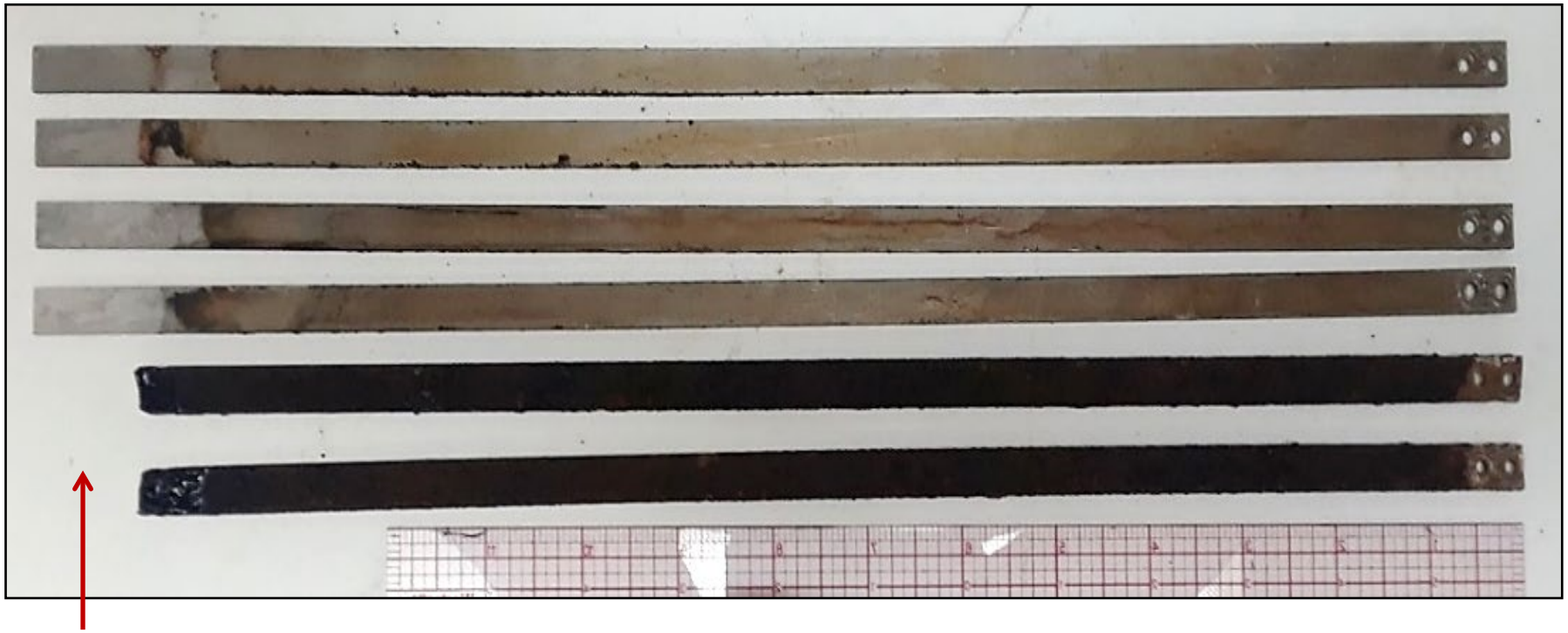
Samples Exposed At NREL At ~10°C Showed Varying Degrees Of Attack

For the samples exposed in the cooled room, the 2¼ Cr samples showed heavy reaction products in the top quarter of the samples while the portion of the 316L samples in the vapor space showed no evidence of reaction products

After Light Cleaning, It Appeared Only ~3cm Of Each Sample Was Immersed In Bio-Oil

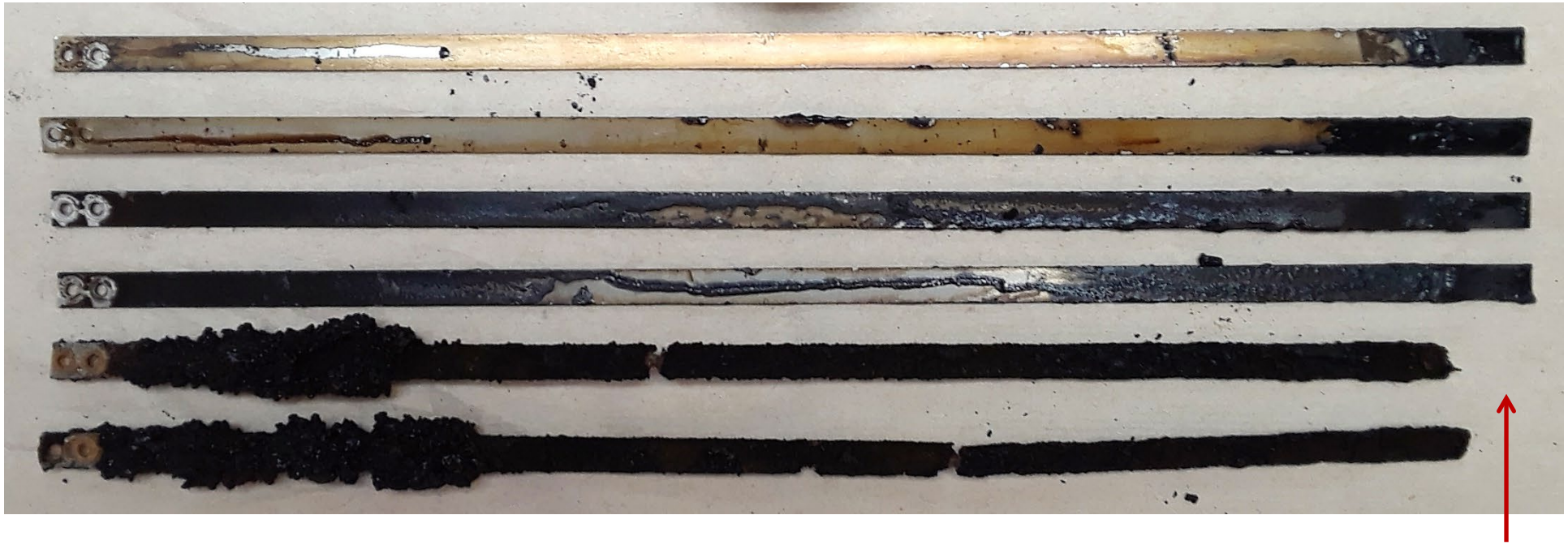


As shown on the left side of the photo, the portion of the 2¼ Cr-1 Mo samples immersed in the bio-oil at ~10°C was completely missing and the surface of the 409 SS sample was roughened

Samples Exposed At NREL At Room Temperature Showed More Extensive Attack

For the samples exposed at room temperature the 2¼ Cr samples showed more severe attack while the portion of the 316L samples in the vapor space showed no evidence of reaction products

After Minimal Cleaning, It Appeared Only ~3cm Of Each Sample Was Immersed In Bio-Oil, And Corrosion Was Significant In The Vapor Space



As shown on the right side of the photo, the portion of the 2¼ Cr-1 Mo samples immersed in the bio-oil was completely missing, and areas in the vapor space were severely thinned

Weight Loss Measurements Showed Weight Loss Decreased With Increasing Cr Content And Increased With Exposure Temperature

Exposure conditions	2 ¼ Cr – 1 Mo steel (2.25% Cr)		409 stainless steel (11% Cr)		316L stainless steel (16% Cr)	
	gm lost	% of original	gm lost	% of original	gm lost	% of original
~10°C	4.8590	10.6	0.1287	0.30	0.0414	0.09
~10°C	4.8819	10.5	0.1303	0.30	0.0331	0.07
Room temp	28.5152	62.2	0.3914	0.91	0.0409	0.09
Room temp	31.0074	67.6	0.3943	0.92	0.0453	0.10

All 4 samples of 2¼ Cr – 1 Mo showed unacceptably high weight losses while the 409 stainless steel samples showed a significant effect of a 10-12 C° increase in temperature. The 316L stainless steel samples had negligible weight losses.

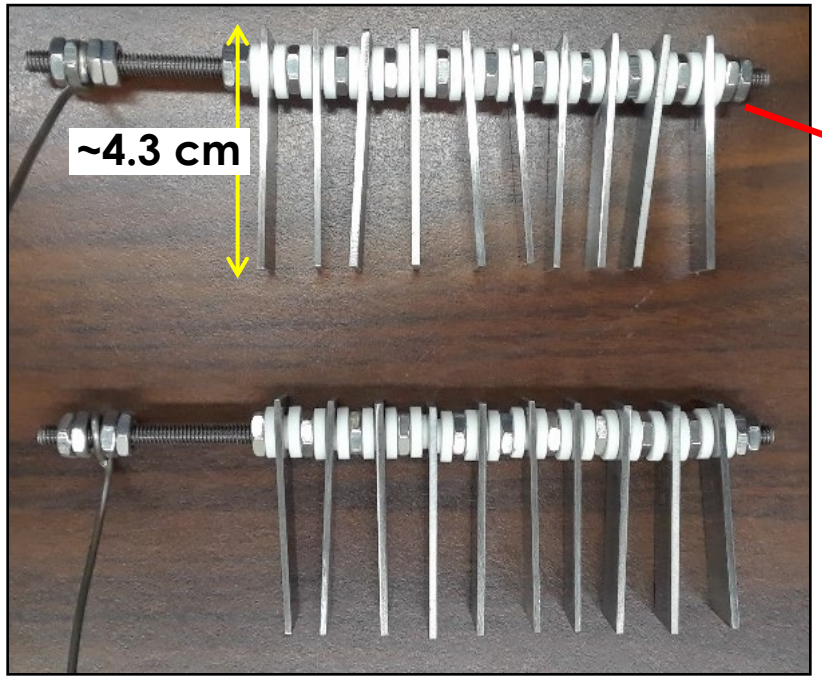
Samples Have Been Exposed In Bio-Oil Under Various Conditions As Well As Diesel Fuel Reference

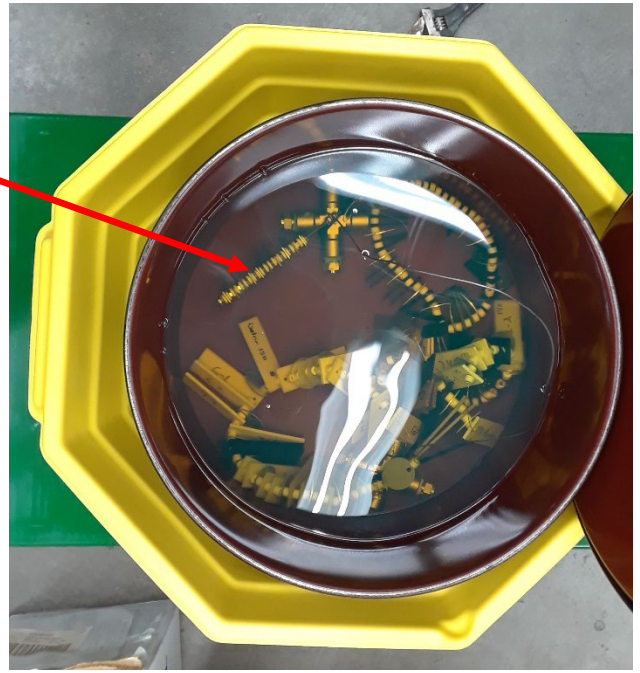
Condition	Sample Materials	Exposure Location	Fluid	Exposure Time (h)	Exposure Temperature
Partial immersion	2¼ Cr-1 Mo, 409 SS, 316L SS	NREL	Fast pyrolysis bio-oil	26,743	~10°C
Partial immersion	2¼ Cr-1 Mo, 409 SS, 316L SS	NREL	Fast pyrolysis bio-oil	26,743	Room temp
Full immersion	**2¼ Cr-1 Mo, 7 Cr-1 Mo, 9 Cr-1 Mo, 409 SS, 316L SS**	**ORNL**	**Three fast pyrolysis bio-oils**	**7,650 & 12,480**	**Room temp**
Full immersion	**2¼ Cr-1 Mo, 7 Cr-1 Mo, 9 Cr-1 Mo, 409 SS, 316L SS**	**ORNL**	**Diesel fuel**	**7,650**	**Room temp**

Additional Materials Were Included In Long-Term Exposures At ORNL

- In each drum, duplicate samples of 2¼ Cr-1 Mo, 7 Cr-1 Mo, 9 Cr-1 Mo, 409 SS and 316L SS were exposed
- Exposures were conducted at room temperature in drums containing three different pine-derived bio-oils and one drum containing diesel fuel
- Two bio-oil exposures were for 12,480 h while the third bio-oil and the diesel fuel exposure were for 7,650 h
- Results reported are for one of the 12,480 h bio-oil exposures and the diesel fuel exposure for 7,650 h

Four Racks Of Samples Like Those Shown Were Exposed In Drums At ORNL





Samples were exposed at room temperature in drums of bio-oil derived from loblolly pine residue or in a drum of diesel fuel. The picture on the right shows the samples in diesel fuel along with racks of nonmetallic samples.

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Weight Change Measurements Showed Negligible Loss By Samples Exposed In Diesel But Significant Losses In Bio-Oil

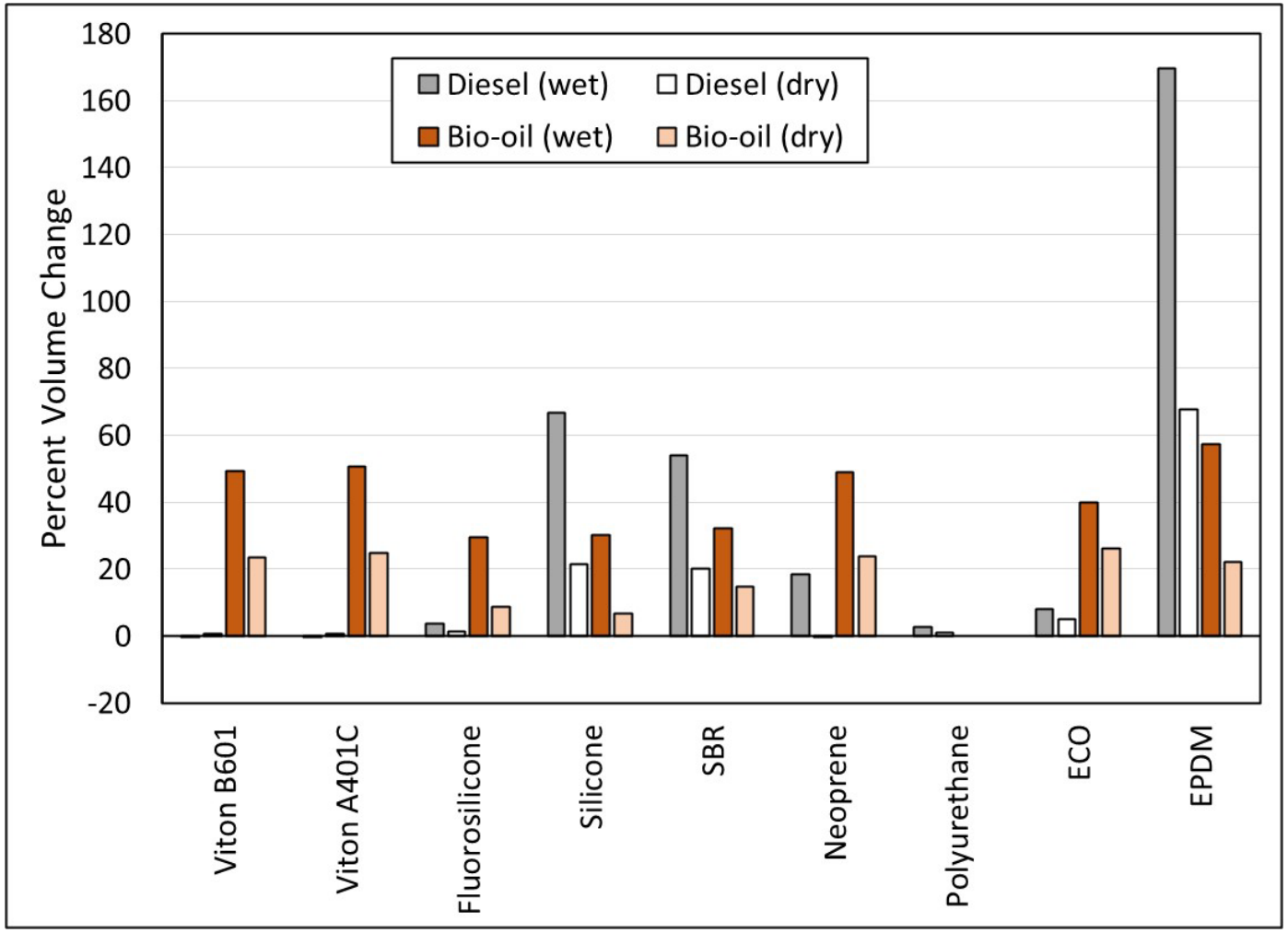
	2¼ Cr-1 Mo		7 Cr-1 Mo		9 Cr-1 Mo		409 stainless		316L stainless	
	mg lost	mm/y	mg lost	mm/y	mg lost	mm/y	mg lost	mm/y	mg lost	mm/y
Diesel	16	<0.01	<1	<0.01	<1	<0.01	<1	<0.01	<1	<0.01
Diesel	3	<0.01	<1	<0.01	<1	<0.01	<1	<0.01	<1	<0.01
FP bio-oil	1,476	0.18	2,442	0.30	3,100	0.38	1,329	0.16	3	<0.01
FP bio-oil	1,609	0.19	2,612	0.32	2,687	0.33	1,354	0.16	1	<0.01

X-ray diffraction measurements identified phases on the surface of several corroded samples

	2¼ Cr-1 Mo steel	2¼ Cr-1 Mo steel	7 Cr-1 Mo steel	7 Cr-1 Mo steel
Material detected	Iron formate hydrate, iron	Iron formate hydrate, iron	Iron formate hydrate, iron	Iron

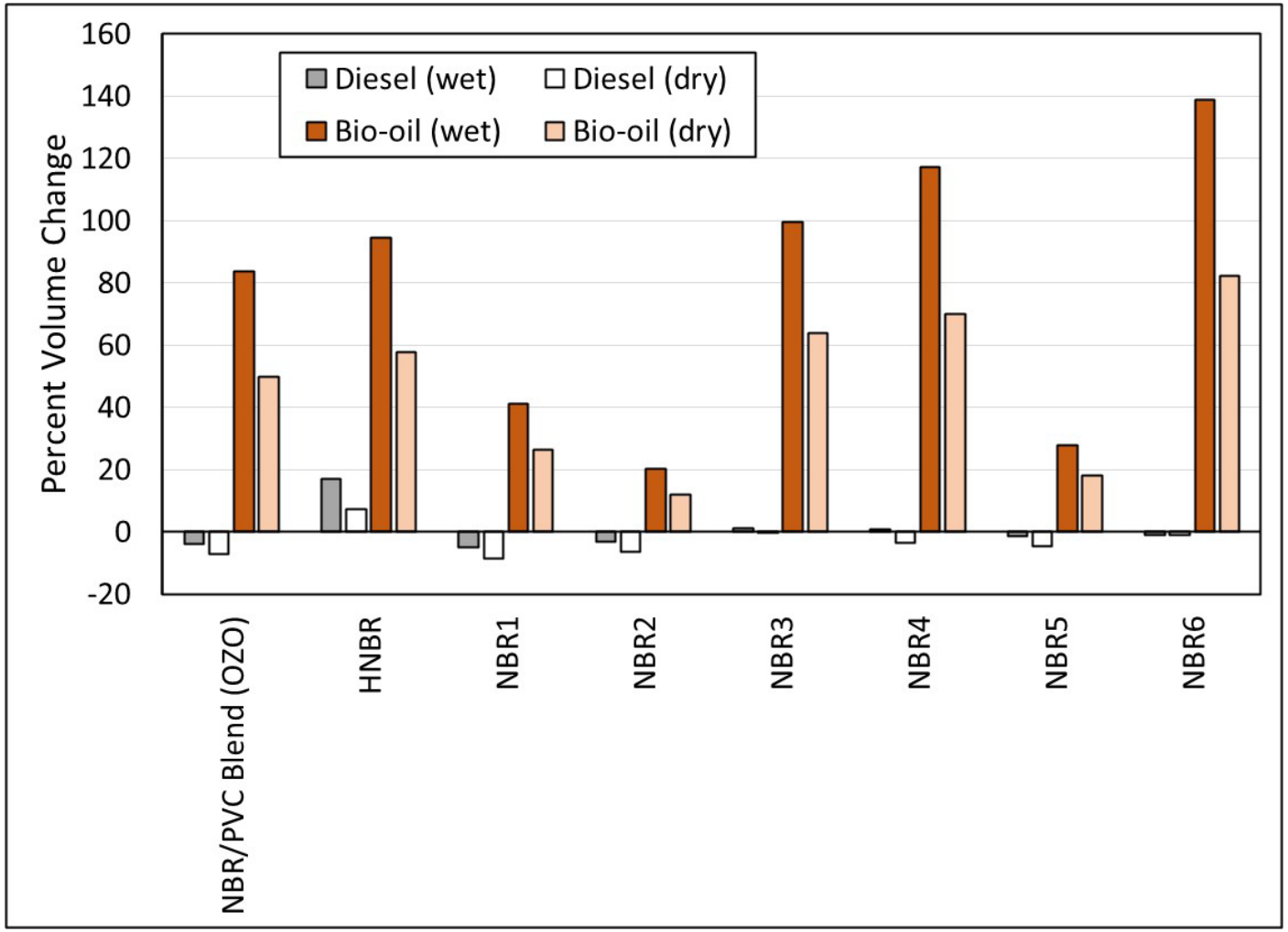
Exposure studies were conducted on infrastructure elastomers with a low-ash high moisture feedstock bio-oil

- Similar to previous bio-oil exposures, excessive swelling noted for fluorocarbons, epichlorohydrin rubber (ECO) and neoprene.
- Reduced swelling (or improved performance) was noted for silicone, styrene butadiene rubber (SBR) and ethylene propylene diene monomer (EPDM)
- Polyurethane underwent partial dissolution with the bio-oil



Nitrile Rubbers Also Exhibited Swelling With The Bio-Oil

- Relatively low swelling was noted for NBR2 and NBR5
- NBRs were heavily compounded with additives (>45% of material was additives)
- NBR or acrylonitrile butadiene rubber performance is highly engineered. The relative levels of acrylonitrile to butadiene influences performance.



Summary

- Long term exposure of metallic samples in bio-oil at ≤50°C shows significant corrosion in alloys with < 11.5% chromium
- The corrosivity of the bio-oils increased with increasing exposure temperature
- Formic acid has been identified as a major contributor, but possibly not the only contributor, to corrosion during transport and storage conditions
- For the as-produced bio-oils used in this study, the acid content was reported to be significant, so more expensive higher chromium alloys will be required for long term storage of these bio-oils

Acknowledgments

- Funding for these studies was provided by DOE's Bioenergy Technologies Office
- Others making a contribution to these studies include Victoria Cox, Maggie Connatser, Ercan Cakmak and Ray Hansen

Thanks for your attention – I will try to answer any questions you have