

Corrosivity of Crude Pyrolysis Oils Made from Different Feedstocks on Transportation and Storage

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ABSTRACT

Crude pyrolysis oils can be produced from different forest and agriculture feedstocks via fast, intermediate or slow pyrolysis processes. Although the oils have promising potential for clean energy production, their corrosivity remains as one of the critical challenges for various industrial applications. A number of studies have been done to investigate the corrosion of metallic materials in crude pyrolysis oils and some general conclusions are made. However, the available information is insufficient for the development of Standards and requirements on the safe oil transportation and storage. To fill some knowledge gaps, this study characterizes the corrosivity of a fast pyrolysis oil produced from hardwood and identifies the corrosion modes and extents of typical iron-based steels (carbon steel, low-alloyed steel and stainless steel), which are cost-effective constructional materials used for the storage and transportation of conventional fossil fuels, under simulated operating conditions of crude bio-oils. Corrosion rate measurements results indicate that carbon steel UNS K02700 experiences active corrosion, low-alloyed steel UNS K91560 suffers less severe corrosion, while stainless steel UNS S31603 shows acceptable resistance. Surface roughness from SEM images matches corrosion observations. Chromium is the dominant element in determining corrosion resistance of steels. A thin layer of Cr oxides shall form on UNS S31603 which prevents the steel from acid attack.

Key words: corrosion, crude pyrolysis oil, iron-based steels, transportation and storage

INTRODUCTION

Due to the depletion of fossil fuel resources and the environmental problems caused by combusting fossil fuels, renewable energy sources have been extensively explored to reduce the emission of greenhouse gases and environmental pollution. Approximate 15-20% of world total energy is provided by renewable energy including solar, biomass, hydropower, wind, ocean energy, geothermal and etc., in which biomass has gained increasing attraction due to its flexibility, availability and environment friendly nature.¹⁻³ Canada has vast biomass resources especially the waste biomass from forestry and agriculture industries as well as municipal wastes which can be converted to bioenergy via mostly thermochemical or biochemical routes.⁴ Among the proposed conversion methods, fast pyrolysis is a significant thermochemical conversion technique to produce liquid biofuels. In this process, biomass feedstock is heated at a rate of 10-200 °C/s to a high temperature (in the range of 400-550 °C), and the vapors are rapidly quenched to yield bio-oils (50-85%).⁵ Commercial operations on the production of bio-oils using fast pyrolysis of forestry and agriculture residues have been realized with a feeding capacity up to 10 ton/h, and the produced liquid oils can be used as fuels, food additives and pharmaceuticals precursors.^{5.}

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Fast pyrolysis bio-oils contain considerable amounts of organic acids with pH values of 2 - 3, leading to safety concerns on the selection of constructional materials for oil storage and transportation. Some corrosion tests have been conducted to measure the susceptibility of various steels and alloys to bio-oils. These studies found that mild steels exhibited remarkable weight loss, especially in the oils with more water at elevated temperatures.⁷ Also there seems to be a critical temperature above which the corrosion damage in the oils likely reduced.^{8, 9} The corrosion rate increased with time at the beginning of contact, and tended to be stable at extended time.^{9, 10} X-ray photoelectron spectroscopy (XPS) results revealed that non-protective layers of oxide and/or hydroxide formed on the surface of UNS G10450.⁸ Therefore, the stable corrosion rate might be a result of the equilibrium between the formation and dissolution of these surface layers, and high temperature possibly shortens the time to reach the equilibrium. The pyrolysis oils produced from agriculture biomass exhibit lower acidity than those from forestry wood, resulting in less corrosion susceptibility.^{11, 12} Compared to a mixed acid solution (0.32% formic acid and 1.70% acetic acid), real bio-oil with same acid concentrations showed reduced corrosivity to metals, suggesting that some components in pyrolysis oil might hinder the access of acids to metals probably due to competitive interactions.¹³

In terms of materials chemical composition, the alloys with high carbon content and low chromium content are deemed to suffer severe corrosion.¹⁴ On the contrary, the corrosion rates of UNS S30400, UNS S31600 and UNS N08024 exhibited lower than 0.01 mm/year even after 15 days immersion in bio-oils at 80 °C;¹⁵ these materials are considered resistant to corrosion.¹² Moreover, high nitrogen alloyed tooling steels were found to show good corrosion resistance to pyrolysis oil, with corrosion rates < 4 µm/year.¹⁴

Despite of the above findings, significant knowledge gaps exist on the selection of cost-effective constructional materials for the safe transportation and storage of bio-oils.^{11, 15-17} For example, pitting was observed on UNS S42200, and through-wall cracking was seen on the U-bend samples of carbon steel and UNS K21590 samples, raising a concern of stress corrosion cracking. For carbon steel, the weight loss could be attributed to Fe and its oxides (Fe₂O₃ and Fe₃O₄) reacting with the organic acids in bio-crude. For stainless steel, on the other hand, the corrosion performance relies on the formation of surface Cr-enriched oxide layer which resists to the oil attack. The question is whether there is a critical content of Cr and/or other alloying elements in a steel for the formation of a protective surface scale to the crude bio-oil at operating temperature (<100 °C). Thus, this paper investigates the corrosion modes and extents of typical constructional materials (carbon steel, low-alloyed steel and stainless steel) in crude pyrolysis oil for short term exposure (7 days). It is anticipated to advance related mechanistic understanding of how materials corrode in crude bio-oils.

EXPERIMENTAL PROCEDURE

Sample Preparation

Testing sample coupons (carbon steel UNS K02700, low-alloyed steel UNS K91560 and stainless steel UNS S31603) with the dimension of 20 mm long × 10 mm wide × 3 mm thick were machined from commercial plates. A small hole with 2 mm radius was drilled on each coupon. The chemical compositions of samples are listed in Table 1.

Table 1
Chemical Composition of Testing Materials in wt% (Balance Fe)

UNS	C	Mn	P	S	Si	Cr	Mo	Ni	Cu	N
K02700	0.167	1.15	0.008	0.007	0.34	0.036	0.014	0.028	0.03	
K91560	0.109	0.47	0.024	0.002	0.33	8.36	0.9	0.07		
S31603	0.02	1.1	0.0285	0.001	0.02	16.4	2.8	13		0.1

All testing coupons were polished with SiC papers up to 600 grit. Deionized water was used during polishing to remove possible contaminations and defects introduced by coupon machining. Polished coupons were cleaned in an ultrasonic ethanol bath for 10 minutes, and then dried using compressed air. Each prepared coupon was stamped with an ID. Prior to immersion testing, the freshly prepared coupons were weighed using a micro-balance with the precision of 1 µg and measured using a digital caliper with the precision of 0.01 mm.

Immersion Test

The pyrolysis oil corrosivity test was based on the NACE standard TM0169/G31. A 2L kettle was filled with 1L bio-oil produced from fast pyrolysis of hardwood sawdust at a Canadian national laboratory. The properties of the pyrolysis oil are shown in Table 2. Two coupons of each steel were used for the immersion test. As shown in Figure 1, testing coupons were suspended in pyrolysis oil by using Teflon strings and separated with plastic spacers. The kettle was placed in a 60 °C water bath. A thermocouple was inserted in the oil to monitor the oil temperature. A condenser was used to condense the oil vapor with cooling water. Nitrogen gas was employed to maintain a deaerated atmosphere in the kettle. Multiple gas outlets were located at the bottom of the kettle to achieve better gas distribution. After 10 min purging, the nitrogen flow was finely tuned by a needle valve to avoid vigorous aeration. After 7 days of submersion, the samples were removed from the kettle and rinsed with ethanol. After air dried, the coupons were weighed using the microbalance mentioned above.

Table 2
Physicochemical Properties of Pyrolysis Oil

Parameter	Value	Unit	Test Method
Density @ 20 °C	1158	kg/m ³	ASTM D4052
Kinematic viscosity @ 40 °C	37.515	cSt	ASTM D445
pH	3.5	NA	In-house
Water content	19.4	wt%	ASTM E203
Heat of combustion	5708.4	Cal/g	ASTM D240
Carbon	55.6	wt%	Modified ASTM D5291
Hydrogen	9.37	wt%	Modified ASTM D5291
Nitrogen	0.42	wt%	Modified ASTM D5291
Oxygen	34.5	wt%	Measured by difference
Ash content	0.07	wt%	ASTM D482
Solid content	0.19	wt%	ASTM D7579