

Corrosion and Chemical Characterization of Bio-Oils from Biomass with Varying Ash and Moisture Contents

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ABSTRACT

As part of the Feedstock Conversion Interface Consortium four samples of pine chips (all combinations of low and high moisture and ash content) were collected and processed for fast pyrolysis. The prepared biomass samples were liquefied at the National Renewable Energy Laboratory (NREL) using the fast pyrolysis process. Following some characterization of the bio-oils at NREL, the bio-oils were shipped to Oak Ridge National Laboratory (ORNL) for corrosion testing and further characterization.

The content and composition of ash in each bio-oil was determined. Corrosion testing consisted of exposing selected metallic and elastomer samples for 1000 hr at 50°C and for longer times at room temperature as well as electrochemical impedance spectroscopy measurements to assess relative corrosivity of the bio-oils. Chemical characterization was conducted to identify the corrosive component of the bio-oils as well as to define the chemical differences among the oils. It was hypothesized that there could be a catalytic effect from the higher ash content in two of the biomass sources. Results of these characterization and corrosion studies will be reported.

Key words: bio-oil, bio-oil corrosion, biomass ash analysis, bio-oil analysis

INTRODUCTION

Use of liquid fuels produced from biomass is an attractive option for significantly reducing production of greenhouse gases compared to combustion of fossil-derived fuels. Thermochemical approaches to bio-oil production, including fast pyrolysis, hydrothermal liquefaction and catalytic fast pyrolysis, are being studied extensively and show great potential. However, the significant oxygen content of biomass results in the bio-oils being quite acidic.

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Considerable effort has been directed at chemically characterizing bio-oils, determining their corrosivity and identifying structural materials that are not degraded by these bio-oils^{1,2}.

This past year an unusual combination of events resulted in four samples of pine derived biomass being processed at Idaho National Laboratory (INL) in preparation for pyrolysis. Then these processed biomass samples were transported to NREL where they were used to produce four fast pyrolysis bio-oils. Samples of the processed biomass were also sent to ORNL for characterization. The bio-oils were produced in significant quantities, and considerable fractions of each were shipped to our lab for further chemical characterization of the bio-oils and for use in corrosion tests. Not only were the individual bio-oils chemically characterized and used in corrosion tests, one of the fractions was used for blending with a heavy fuel oil (HFO). These blends were used for corrosion testing as well as chemical characterization. This is thought to be the first time that raw biomass was characterized, followed through the liquefaction process and then subjected to corrosion testing and more thorough characterization.

RESULTS AND DISCUSSION

Biomass Characterization

Biomass is a relatively easily obtained feedstock source for production of liquid fuels by any of several production processes. In order to prepare the biomass to be introduced as feed for the liquefaction processes, the biomass needs to be reduced in size so that it can be more easily handled and introduced into the liquefaction vessels. This requires mechanical grinding and chopping of the biomass with the attendant wear and degradation of the size reduction equipment that includes bale grinders, hammer mills, rotary shear cutters and plug screw feeders. This degradation of materials results in lost production time and additional expense for replacement parts and installation of the parts. Instrumental in the degradation of the grinding and chopping equipment is the ash, both extrinsic and intrinsic, that is contained in the biomass. Much of the extrinsic ash is introduced during the biomass harvesting operation while the intrinsic ash is basically incorporated as a component of the biomass.

The baseline biomass processing runs conducted at INL utilized loblolly pine whitewood as the low ash biomass source and loblolly pine residues (branches, bark, needles) as the high ash biomass source. It is not surprising that the residues had the highest ash content since, among the various fractions of a pine tree, the bark contains the highest amount of extrinsic ash and the second highest amount of intrinsic silica. An even higher amount of intrinsic silicon was found in the needles. Determination of the total ash concentration is a somewhat controversial issue in that the conventional approach involves burning the biomass and collecting the inorganic material that remains. Any component of the biomass that will form an inorganic compound during combustion will be considered to be an ash component. Consequently, materials that are not initially present as an inorganic compound could be converted to an oxide and then counted as part of the extrinsic ash component.

An alternate means to determine the extrinsic ash content was developed in our laboratory and will be described in greater detail in an upcoming report³. Basically, the biomass is placed in deionized water and sonicated to separate the extrinsic ash from the organic constituents of the biomass. The lower density organic material floats to the surface and can be removed by a strainer. The higher density ash can be dried and collected. The elemental components of the ash can be determined using the energy dispersive spectroscopy system on a scanning

electron microscope, and X-ray diffraction can be used to identify the compounds making the major components of the ash.

Ash collected from both low-ash and high-ash biomass samples showed oxygen, silicon, aluminum and iron as the major components with silica and alumina as the dominant compounds in both types of ash. Figure 1, which is taken from reference 3, shows the relative abundance in wt % of the major components, and it is clear that oxygen and silicon are the primary elements in the ash. Even though iron is present in significant amounts, since the graph shows weight percent, the concentration of iron containing compounds will be considerably less than those containing the lighter elements silicon and aluminum. One question related to the ash components is whether the presence of ash with a different composition or in a larger amount might provide a catalytic effect. The ash analysis indicates there is not a meaningful difference in the ash composition between the “low ash” and “high ash” samples.

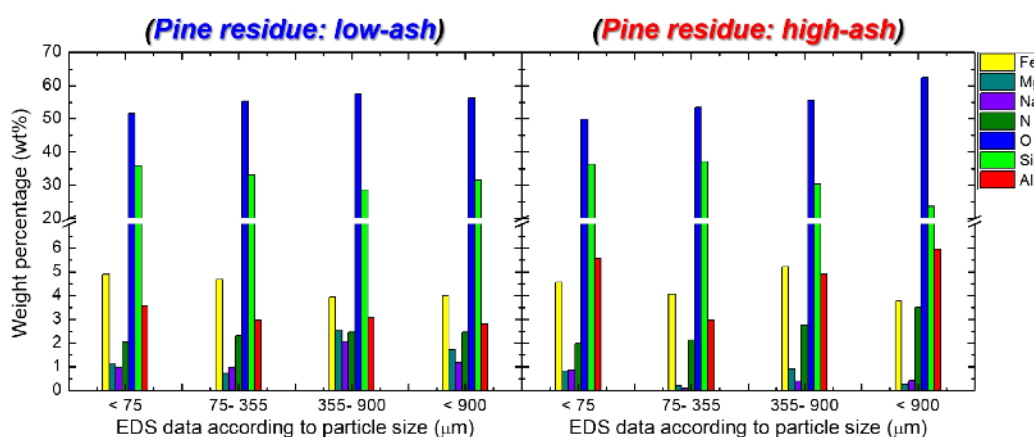


Figure 1 Graphical comparison of the chemical composition of low-ash and high-ash pine residue – from reference 3.

Chemical Characterization of Bio-Oils

The four variations of pine derived biomass, identified as Low Ash Low Moisture (LALM), Low Ash High Moisture (LAHM), High Ash Low Moisture (HALM) and High Ash High Moisture (HAHM), were provided to NREL for processing in their Thermal and Catalytic Process Development Unit using the fast pyrolysis process. The bio-oils produced were analyzed by that laboratory's staff, and the results of their analysis are shown in Figure 2⁴. From this figure, it would appear that the high ash bio-oils had slightly greater acid content, lower aldehyde and lower sugar content. In almost all cases (except for paraffins) the concentration of each product was higher in the high moisture samples than in the low moisture samples. These seem to be very consistent trends, but the sample size is small enough that it would not be appropriate to draw any firm conclusions.

Analyses of the four bio-oils were also conducted in our laboratory, and the results are shown in Table 1 and displayed in Figures 3-4. Formic and acetic acids were determined via capillary electrophoresis with indirect UV-visible absorbance detection. For methoxymethyl phenol and disaccharide, direct sampling via thermal desorption in an inert environment, followed by gas chromatography with electron ionization mass spec detection was carried out. "AMTAN" is