Short Communication

Measuring Bio-Oil Upgrade Intermediates and Corrosive Species with Polarity-Matched Analytical Approaches

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1.0 Abstract

Integrating biofuels with conventional petroleum products requires improvements in processing to increase blendability with existing fuels. This work demonstrates analysis techniques for more hydrophilic bio-oil liquids that give improved quantitative and qualitative description of the total acid content and organic acid profiles. To protect infrastructure from damage and reduce the cost associated with upgrading, accurate determination of acid content and representative chemical compound analysis are central imperatives to assessing both the corrosivity and the progress toward removing oxygen and acidity in processed biomass liquids. Established techniques form an ample basis for bio-liquids evaluation. However, early in the upgrading process, the unique physical phases and varied hydrophilicity of many pyrolysis liquids can render analytical methods originally designed for use in petroleum-derived oils inadequate. In this work, the water solubility of the organic acids present in bio-oils is exploited in a novel extraction and titration technique followed by analysis on the water-based capillary electrophoresis (CE) platform. The modification of ASTM D664, the standard for Total Acid Number (TAN), to include aqueous carrier solvents improves the utility of that approach for quantifying acid content in hydrophilic bio-oils. Termed AMTAN (modified Total Acid Number), this technique offers 1.2% relative standard deviation and dynamic range comparable to the conventional ASTM method. The results of corrosion product evaluations using several different sources of real bio-oil are discussed in the context of the unique AMTAN and CE analytical approaches developed to facilitate those measurements.

Keywords: biomass, capillary electrophoresis, Total Acid Number, pyrolysis oil upgrading, carboxylic acid, corrosion

2.0 Introduction

In view of the increasing consumption of petroleum-based fuels and chemicals, combined with decreasing supplies and enhanced domestic and international emphasis on renewable energy sources, biomass-based fuels and bio-oils offer a promising alternative. [1,2] However, converting fuel crops to bio-oils involves several layers of technical complexity, both within a single process (chemical mechanisms of enzymatic or thermochemical catalysis, for example), and spanning the full field-to-fuel set of unit operations. One example of such a pathway is the conversion via pyrolysis of wood to energy liquids.[3] One important aspect of this conversion process is the infrastructure, including metals and sealing materials, used during processing, storage and transport of bio-oil liquids at various stages of upgrade. Characterization of biomass products is generally important because it determines the improvement made by the biomass upgrading process and, specific to the research described here, ultimately paves the way for selection of materials for bio-oil processing and storage infrastructure that allow achievement of technoeconomic goals. [4] An increased understanding of the composition of bio-oils will ultimately allow increased blendability with existing fuels and reduced expenses of upgrading and infrastructure. [5] Specifically, accurate determination of acid content and representative chemical compounds will allow assessment of both the corrosivity and the progress toward removing oxygen and acidity in bio-oil upgrading. [6-8] The unique physical phases and varied hydrophilicity of many pyrolysis liquids opens up opportunities to apply analytical methods novel to the field of oil analysis and method modifications to complement the most prevalent methods currently used, such as viscosity, water content, elemental analysis, and gas chromatography, as well as other peripheral

methods of liquid chromatography and optical spectroscopies. [9 – 12] In this work, the modification of ASTM D664, the standard method used for Total Acid Number (TAN) [13], to include aqueous carrier solvents improves the utility of that approach for quantifying acid content in hydrophilic bio-oils. Utilization of a novel separation methodology developed on a capillary electrophoresis (CE) system, an aqueous, high-efficiency chromatography separation platform, allows determination of formic, acetic, and other organic acids in bio-oil liquids, as well as inorganic anions that can also be involved in corrosion, such as chlorine, sulfate, and phosphate. [14]

The objective of the work described is to characterize biomass intermediates and products using current and developing techniques in order to understand potential chemical barriers such as corrosive species, hydrophilicity, and reactive components and intermediates in order to elucidate and mitigate mechanisms of corrosion and upgrading barriers. It is informally admitted in the biomass upgrading and handling communities that the ASTM method for determination of TAN for petroleum liquids is non-ideal for bio-oil liquids, due in large part to the immiscibility of more multi-phasic and hydrophilic components of bio-oils with the titration solvents used in that method, including isopropanol and toluene.[13] Even the International Energy Agency's round robin study of 2012, headed by the widely respected teams of Elliott and Oasmaa, concedes, "other analyses (Table 9) including ash, TAN (total acid number), pH, and carbonyl content. The numbers in the several categories show a consistency in scale, but they also suggest a large variability in the reproducibility from one lab to another." [15] Several laboratories have put forth useful modifications of the TAN titration and calculation. [6, 10, 13, 15-18] Table 1 serves as a sampling of these. In surveying current research publications in areas other

than strict speciation but that deal with some analysis, it was found that several different approaches to titrating for total acid number exist. [6, 10, 13, 15-18] These differences rely on changing titration solvents, but only recently is an effort being made via a round robin test set being funded by the U.S. Dept. of Energy's Bioenergy Technologies Office (U.S. DOE – BETO) and headed by Idaho and Pacific Northwest National Laboratories to validate standardization of four tests for bio-oils. For total acid content, the study will assess a set of titration solvents that might adequately span the hydrophilicity – hydrophobicity range encompassed by the myriad bio-oil liquids being assessed, as well as comparing inter-lab results from NMR, GC-MS, and carboxylic acid titration. Besides defining solvent ranges, using specialized pH electrodes such as in the Ross electrode-mediated titration of fuel ethanol's TAN, could offer redress for the as-yet loosely and variously defined area of bio-oil acid content.[19, 20]

Table 1: Representation of various research approaches to measuring total acid content of a bio-oil liquid.

The work described herein begins with one more approach to extraction and solvent matrix. From the whole-acid quantification, it became obvious that further speciation of hydrophilic and semi-polar bio-oil constituents was warranted. In this context, the water-friendly, high efficiency separation technique of capillary electrophoresis (CE) was introduced and standards were used to verify qualitative and quantitative analysis of organic acids in the bio-oil liquids, including acetic acid, formic acid, and larger molecular weight carboxylic acids, as well as inorganic anions. Our

approach to developing analysis techniques was a combination of innovation and modification. Borrowing from the petroleum energy industry, [21] new approaches were developed to accommodate polarity and oxygenation.[7] The technique of CE offers extremely high separation efficiency. [22] This high efficiency comprises a high capacity for separating myriad different compounds as well as a high chromatographic resolution required to achieve more complete separation of those compounds. [14] CE has been added to the stable of traditional analytical chemistry techniques over the last 25 years, mainly due to its extremely high chromatographic efficiency, low sample requirements, mobile phase tailorability, and ready applicability to aqueous samples. [23] However, its utilization in the realm of hydrocarbon fuel studies has been limited chiefly to separating high molecular weight carcinogens such as polycyclic aromatic hydrocarbons (PAHs) via micellar electrokinetic capillary chromatography. [24] The majority of the work described is based on indirect ultraviolet absorbance detection to identify formate and acetate levels in the bio-oil extracts. Finally, this research led to the next steps currently under way using the CE separation hyphenated to electrospray ionization mass spectrometry (ESI-MS), with the structural characterization power to elucidate chemical definition of the larger molecular weight organic acids in bio-oil. [25,26] This will be reported in a subsequent publication.

3.0 Material and methods

3.1 Biomass Sources

This work was performed, with the exception of the Iowa State red oak samples, on substrates of unknown provenance, for which the chain of custody is not known. The species and the cultivars cannot be specified and while the authors BELIEVE that this work exemplifies the difference between materials - there is a reasonable concern that there may

be substrate factors that influence the results obtained. In the case of red oak bio-oils obtained from Iowa State University's fractional pyrolysis unit originated from *Quercus rubra* supplied by Wood Residual Solutions, LLC of Montell, Wisconsin, USA. Pyrolysis was carried out at partner labs, as noted in the Table 2 below, with the understanding that extensive sample source description was not required.

Table 2: Through collaborations, a variety of pyrolysis oil samples from university, commercial, and national lab sources were studied. *Denotes international collaboration.

3.2 Aqueous Modified Total Acid Number (AMTAN)

A mass of sample is measured into a borosilicate glass, EPA-solvent certified vial. That mass is recorded and then a mass of deionized water is added to create approximately a 10% mass combination of bio-oil in water. The sample is placed in an ultrasonic bath for 40 minutes. The sample is then filtered with a PTFE syringe tip, 220 nm pore filter into a clean certified vial. That sample, which is homogeneous due to filtration of any post-sonication agglomerations of hydrophobic, non-polar oils, is then titrated with a standardized KOH solution using an Accumet Basic AB15 pH meter from Fisher Scientific, Waltham, MA, USA. The standardization solution for the KOH was sulfuric acid in water, at 24.1767 parts per thousand, bought as a standardization reagent from Sigma Aldrich, Inc., St. Louis, MO, USA. All other reagents were purchased from Sigma Aldrich and used as received.

3.3 Capillary Electrophoresis

Separations were carried out on a capillary electrophoresis instrument from Agilent Technologies, Inc., Santa Clara, CA, USA, using the proprietary CElixir OA, a mobile

phase/buffer mixture available from MicroSOLV, Inc., Eatonville, NJ, USA. This creates a dynamic coating on the capillary wall and maintains a constant level of background chromophore, detected with ultraviolet absorption at 237 nm. Only migrating anions, such as formate or acetate, displace some amount of chromophore, creating a negative-direction peak in the electropherogram trace. Capillary was 75 micrometers inner diameter, 365 micrometers outer diameter, 65 cm total length, with 50 cm to the detection window. The capillaries were obtained from Polymicro, Inc., Mountain View, CA, USA, and were pretreated with water, ethanol, and sodium hydroxide solutions prior to buffer filling, flushing, and conditioning for each run. Injections were made using 5000 Pa head pressure for 5 seconds, with separation voltage of 30kV. The capillary was stored full of water between batches of runs to extend its functional life. Samples were prepared for CE by carrying out an equal-volume hexane rinse on the titrated aliquots created during calculation of AMTAN. This step insured that minimal residual uncharged compounds were injected onto the capillary to interrupt the conductive liquid path or form a physical blockage. Standard solutions of mixed acids (formic and acetic), titrated to pH 10 were injected, and those peaks' integrated areas were used in quantifying the integrated area counts for acetic and formic acids in samples of bio-oils. Dilutions of 1:10 titrated sample in deionized water were employed in cases where the as-titrated AMTAN bio-oil sample was too concentrated to fall within the linear response range of the CE chromatographic and spectroscopic techniques. In preliminary comparisons between amount of acids known and unknown, a common response factor to the indirect UV absorption detection technique was used, although quantitative results for the known organic acids formic and acetic from CE were based upon standard injections of standards of those same compounds.

4.0 Results and Discussion

Biomass processing technologies offer renewable sources of fuel, power, and chemicals; these processes can produce several different chemical groups ranging from water soluble organic acids, alcohols, ketones, and aldehydes to non-water soluble aromatic, olefinic and paraffinic compounds. [27-30] This results in a challenging variety of products arising from the pyrolytic processing of biomass from a variety of sources, which proves somewhat intractable if only established (non-novel) extraction methods are applied. A combined suite of novel aqueous extractions, titrations, and separations is described to address the varied nature of these products.

For analyzing the corrosion capacity of various bio-oil samples, we devised a method comprised of water-based modified total acid number titration that addresses the most hydrophilic components and weak organic acids of pyrolysis liquids. Beyond providing a total acid content measurement, the water modification to the ASTM D664 Standard for total acid number also serves as a sample preparation step for CE. The modified method works well on most of the samples of low- to medium-upgrade quality, and is required because the ASTM method prescribes using a titration carrier solvent for the base (potassium hydroxide) that is immiscible with the hydrophilic oils and/or oil components. This immiscibility means false reading of "N/A", "0", or an overestimation of TAN, based on the titration of the large amount of phenols titrated and included in the total acid number when using the ASTM method. Figure 1 conveys analytical figures of merit for the techniques, namely reproducibility for AMTAN, and linear dynamic range and precision for CE of formic and acetic acids. Table 3 demonstrates the disconnect between the existing method and our method modified to accommodate the oxygenation and hydrophilicity of

some bio-oil samples. However, higher upgrade products that resemble more the hydrocarbon content, and therefore the hydrophobicity, of more standard petroleum liquids, are less accessible by the AMTAN method described.

Figure 1: Top panel contains data used to determine precision of AMTAN method. In the bottom panel, the chart indicates standard curves for determining the linear dynamic range and precision of the CE method, where three separations were performed for each of three different standard solutions of formic and acetic acid.

Table 3: A comparison of results from the AMTAN approach herein returned more reproducible values than the standard ASTM method. The AMTAN method accommodates the increased hydrophilicity of pyrolysis oil liquids and serves as a preparatory step for CE analysis of formic, acetic, and other organic acids.

Chemical analysis was carried out to determine the acid content and the major organic species present in the pyrolysis liquid samples. With the introduction of new biofuels sourced from feedstocks rife with oxygenated and ionizable compounds, however, the utilization of CE in one of its more traditional forms offers relevant information about organic acid content. Using CE, the prevalence of unidentified organic acids in bio-oil upgrade intermediates has been determined. Also, trends in these values have been evaluated in comparison to $\text{pH}_{\text{initial}}$ and AMTAN. Whereas acetic and formic content dominate most samples shown, data indicates a significant presence of larger organic acids. Figure 2, inset, shows an example where approximately 40% of total acid anions in this bio-

oil sample were larger molecular weight organic acids, assuming a common CE method response factor and based upon standard acetic and formic acids' peak area per mass-based concentration. More quantitative comparison will become available as the UV-vis indirect response factors are defined, which is on-going and relies upon electrospray ionization mass spectrometry (ESI-MS) structural confirmation and introduction of standards for the various families of larger molecular weight acids.

Figure 2: X-ray diffraction analysis (A) of corroded carbon steel sample (B) with surface deposits identifying it as iron formate hydrate, a likely corrosion product formed upon attack of the iron by formic acid. [17] The representative electropherogram (C) shows formic and acetic acid peaks labeled, as confirmed with standard injections. The high-pH CE analysis of pyrolysis oil samples indicates that unknown organic acids ("unk org acids") are also present and could contribute to corrosivity. CE peaks are inverted because indirect UV-visible spectroscopic detection was used on-column.

As one of the aims of bio-oil upgrading is to increase hydrocarbon character of the liquid, it logically follows that further improvements in the bio-oils will lead to a reduced content of oxygenates. Correlations between specific acids determined via CE and the acid species' partial profile of a corrosive bio-oil sample can be made. As shown in Figure 2, a reaction product was observed on the surface of the carbon steel and 2¼ Cr-1 Mo steel, and this layer was removed from several samples exposed in each of the six untreated pyrolysis oils. X-ray diffraction was used to identify the compounds present in the reaction product, and iron formate hydrate was the dominant component as shown in the pattern displayed in

Figure 2. This appears to be a product from reaction of the metallic sample with formic acid in the pyrolysis oil. Iron formate would have hydrolyzed when the samples were exposed at room temperature in moist air.[17] Although the dominant (crystalline) component of the corrosion product is a result of reaction with formic acid, there are many other, higher molecular weight organic acids present in the bio-oil. It is quite possible that some of these other acids would be more aggressive at higher temperatures and some corrosion could occur with the stainless steels. Future tests will be conducted at higher temperatures with partially treated oils; the untreated oils begin to polymerize at temperatures not much above the 50°C test temperature so higher temperature corrosion tests with untreated oils are not feasible.

Figure 3 demonstrates a subset of compiled data that was used in a separate work to study corrosion patterns among a variety of sample origins and treatments. Refer to Table 2 as a key to the labels and feedstocks used to create this cadre of bio-oil samples. Specifically, Figure 3 offers comparison of trends for AMTAN value with trends in formic and acetic acid species quantified via high-pH extraction and titration, followed by CE. This compilation of data for AMTAN allows comparisons among total acid content and major acid species. Such comparisons can allow indirect assessment of how much known acids versus unknown larger or more complex organic acids contribute to total acidity. A direct representation of this indirect comparison of moles H^+ is made by inferring those values from known molecular weights of formate and acetate for the CE values. Moles H^+ are inferred from moles KOH required to titrate each sample to arrive at values for AMTAN. Such compounds as formic acid are speculated to initiate significant general corrosion of even some higher-quality steel materials. The agreement of these three figures of merit (corrosion, acid

species content, and AMTAN), indicates that this combination of relatively simple analyses could offer a robust and predictive first-pass screening approach for both assessing bio-oil processing methods as well as identifying more corrosion-resistant infrastructure materials. The central theme here is that the analysis approaches used are tailored to phase miscibility, maximizing the likelihood that sampling is representative and more information-rich. Selection of appropriate sampling approaches will facilitate identification and the ability to trace the removal or enrichment of corrosive species or fuel precursors, respectively.

Figure 3. Comparison of AMTAN value with formic and acetic acid species quantified via high-pH extraction and titration, followed by CE. Compilation of data for AMTAN allows comparisons among total acid content and major acid species. Such comparisons can allow indirect assessment of how much known acids versus unknown larger or more complex organic acids contribute to total acidity. A direct representation of this indirect comparison of moles H^+ is made by inferring those values from known molecular weights of formate and acetate for the CE values. Moles H^+ are inferred from moles KOH required to titrate each sample to arrive at values for AMTAN.

Future work specific to the research described herein will focus on defining partitioning values of different compound classes into the solvent systems in order to more quantitatively assess representativeness of sampling. Once these parameters are clarified, the bio-oil community can more confidently define upgrading quality and corrosive potential for various bio-oil fractions based on both established and emerging analytical techniques.

5.0 Conclusion

In this work, methods for more quickly and reliably assessing acid contents in semi-hydrophilic bio-oil samples were developed. AMTAN quantities and CE (aqueous platform) chemical speciation will continue to be used in order to more quickly screen lower-upgrade and slightly polar bio-oils for acid content and more fully assess the routes to material degradation. Continued use of the acidic titration followed by non-polar solvent extraction will offer neutral-molecule confirmation of species identification in the base-titrated approaches. By modifying methods borrowed from the conventional energy industry, such as Total Acid Number modified with new extractions and titration solvents, characterization of bio-oil corrosivity was facilitated. In view of the wide variation among pyrolysis liquid qualities, more than one set of titration conditions, tested on oils of a range of upgrade levels, would help the practitioners in the field to gain a meaningful, widely accepted into measuring for "bio-oil Total Acid Number". This type of comparative evaluation and down-selection will be well-accomplished by the fresh round robin study begun in 2014 at NREL and INL, and continued with an expanded list of performer laboratories in 2015.

6.0 Acknowledgements

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Table 1: Representation of various research approaches to measuring total acid content of a bio-oil liquid.

Method Origin	Short Name	Dilution Solvent (Titration Solvent)	Ref
ASTM D664	TAN	Toluene/propanol/water (ethanol)	13
Agblevor (Utah State)	Rapid TAN	Acetone (water)	16
NREL/PNNL	Modified TAN	n/a (TBAOH in propanol with TEABr electrode-filling solution)	6, 10
ORNL	AMTAN	Ultrasonicated water (water)	17
Pollard-Brown (ISU)	MAN	Dimethyl formamide (methanol)	18

Table 2: Through collaborations, a variety of pyrolysis oil samples from university, commercial, and national lab sources were studied. *Denotes international collaboration.

Collaborator	Collaborator Abbreviation	Biomass Type
National Renewable Energy Laboratory, USA	NREL	Oak
University of Massachusetts, USA	Univ Mass	Mixed hardwood
Technical Research Centre of Finland	VTT*	Pine sawdust
Industrial Research Collaborator	Unidentified	Various
United States Department of Agriculture	USDA	Switchgrass
Pacific Northwest National Laboratory, USA	PNNL stabilized	Various
Iowa State University, USA	Iowa State RO, Iowa State CS	Corn stover, red oak
Battelle, Columbus, OH, USA	n/a	Various

Figure 1: Top panel contains data used to determine precision of AMTAN method. In the bottom panel, the chart indicates standard curves for determining the linear dynamic range and precision of the CE method, where three separations were performed for each of three different standard solutions of formic and acetic acid.

Table 3: A comparison of results from the AMTAN approach herein returned more reproducible values than the standard ASTM method. The AMTAN method accommodates the increased hydrophilicity of pyrolysis oil liquids and serves as a preparatory step for CE analysis of formic, acetic, and other organic acids.

Sample	Biomass Source	ASTM D 664*	ORNL AMTAN	Comments
VTT	Pine sawdust	267*	66	*For external validation and to insure method accuracy, ASTM D664 was performed at SGS, Deer Park, TX. For all samples, ASTM D664 results were accompanied by the following report comments: “Results may not be accurate due to the nature of the samples. Results outside the scope of the method. Results varied depending on sample size.”
UMass	Mixed hardwood	303*	108	
RO-1	<i>Quercus rubra</i>	380*	132	
RO-2	<i>Quercus rubra</i>	308*	71	
CS-1	<i>Zea mays</i>	276*	47	
CS-2	<i>Zea mays</i>	110*	78	

Figure 2: X-ray diffraction analysis (A) of corroded carbon steel sample (B) with surface deposits identifying it as iron formate hydrate, a likely corrosion product formed upon attack of the iron by formic acid. [17] The representative electropherogram (C) shows formic and acetic acid peaks labeled, as confirmed with standard injections. The high-pH CE analysis of pyrolysis oil samples indicates that unknown organic acids (“unk org acids”) are also present and could contribute to corrosivity. CE peaks are inverted because indirect UV-visible spectroscopic detection was used on-column.

Figure 3. Comparison of AMTAN value with formic and acetic acid species quantified via high-pH extraction and titration, followed by CE. Compilation of data for AMTAN allows comparisons among total acid content and major acid species. Such comparisons can allow indirect assessment of how much known acids versus unknown larger or more complex organic acids contribute to total acidity. A direct representation of this indirect comparison of moles H⁺ is made by inferring those values from known molecular weights of formate and acetate for the CE values. Moles H⁺ are inferred from moles KOH required to titrate each sample to arrive at values for AMTAN.

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