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Characterization of catalytic fast pyrolysis oils: The importance of solvent selection for analytical method development

Anne E. Harman-Ware, Jack R. Ferrell III*

National Bioenergy Center, National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, United States

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ABSTRACT

Two catalytic fast pyrolysis (CFP) oils (bottom/heavy fraction) were analyzed in various solvents that are used in common analytical methods (nuclear magnetic resonance – NMR, gas chromatography – GC, gel permeation chromatography – GPC, thermogravimetric analysis – TGA) for oil characterization and speciation. A more accurate analysis of the CFP oils can be obtained by identification and exploitation of solvent miscibility characteristics. Acetone and tetrahydrofuran can be used to completely solubilize CFP oils for analysis by GC and tetrahydrofuran can be used for traditional organic GPC analysis of the oils. DMSO- d_6 can be used to solubilize CFP oils for analysis by ^{13}C NMR. The fractionation of oils into solvents that did not completely solubilize the whole oils showed that miscibility can be related to the oil properties. This allows for solvent selection based on physico-chemical properties of the oils. However, based on semi-quantitative comparisons of the GC chromatograms, the organic solvent fractionation schemes did not speciate the oils based on specific analyte type. On the other hand, chlorinated solvents did fractionate the oils based on analyte size to a certain degree. Unfortunately, like raw pyrolysis oil, the matrix of the CFP oils is complicated and is not amenable to simple liquid–liquid extraction (LLE) or solvent fractionation to separate the oils based on the chemical and/or physical properties of individual components. For reliable analyses, for each analytical method used, it is critical that the bio-oil sample is both completely soluble and also not likely to react with the chosen solvent. The adoption of the standardized solvent selection protocols presented here will allow for greater reproducibility of analysis across different users and facilities.

1. Introduction

The rapid, thermal decomposition of biomass in the absence of oxygen can generate a highly oxygenated oil product known as pyrolysis oil [1]. Catalytic upgrading of pyrolysis oil and vapors has been explored using many types of catalysts and conditions including traditional catalytic cracking and hydrotreating methods to deoxygenate the pyrolysis products to yield hydrocarbons, which may then be blended with traditional liquid fuels [2–5]. Upgraded pyrolysis oils, including catalytic fast pyrolysis (CFP) bio-oils and hydrotreated fast pyrolysis oils, have shown significantly different composition and properties from their raw precursor vapors, oils, and starting feedstocks [2–6]. One key difference in the properties of the raw and upgraded pyrolysis oils is that the CFP oils will separate into three layers (Fig. 1): a top, hydrocarbon rich layer, a middle aqueous layer containing organic products and a bottom layer (usually the highest yield) containing

upgraded hydrocarbon products and oxygenated products similar to raw pyrolysis oil. With the difference in composition and physical separation characteristics of the raw and upgraded oils, it is important to consider the differences in the preparation of the oils for analysis by typical analytical techniques. Sample preparation and analytical methodologies used to analyze raw pyrolysis oils may need to be modified for upgraded oils. As with raw pyrolysis oils, analytical techniques need to be standardized such that accurate results can be comparable between laboratories, researchers, and experiments.

The standardization of the techniques used for the characterization of pyrolysis oils has been suggested in books and publications and has been researched, optimized, and modified yet not all researchers use the same techniques, making comparisons across laboratories difficult [7,8]. Recent work has led to several validated analytical methods that quantify chemical species or functional groups in raw pyrolysis bio-oils [9–19]. While this is a big step forward for standardizing the analysis of

Abbreviations: CFP, catalytic fast pyrolysis; DAD, diode array detector; DMSO- d_6 , dimethylsulfoxide- d_6 ; GC/MS, gas chromatography mass spectrometry; GPC, gel permeation chromatography; HPLC, high performance liquid chromatography; LLE, liquid-liquid extraction; NMR, nuclear magnetic resonance; PAH, polyaromatic hydrocarbon; TGA, thermogravimetric analysis; THF, tetrahydrofuran

* Corresponding author.

E-mail address: Jack.Ferrell@nrel.gov (J.R. Ferrell).

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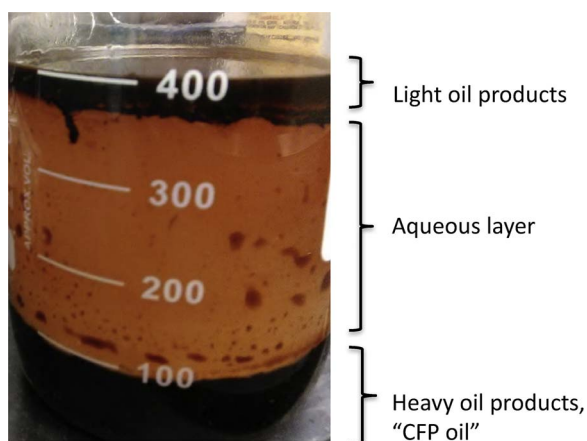


Fig. 1. Catalytic fast pyrolysis oils and aqueous products upon collection (CFP oil 1).

raw bio-oils, upgraded bio-oils such as those from catalytic fast pyrolysis still lack reliable standards. Additionally, the characterization of upgraded pyrolysis oils has often adopted the same techniques, sample preparation, and instrumental set-up as those used for raw pyrolysis oils, along with the lack of official standardization for analysis [3,5,14,20]. ASTM methods have been universally adopted for the physical properties and elemental composition of the upgraded and raw pyrolysis oils. The chemical and functional group composition of pyrolysis oils can be elucidated using GC/MS, GC/FID, NMR, FTIR, IC, GC X GC, titration and LC techniques. However, the preparation of the oil samples and instrumental set-up for these analytical methods varies widely across laboratories and researchers, perhaps due in part to the lack of availability of the accepted methods and resources for performing them. Additionally, given the difference in composition of catalytic fast pyrolysis oils from raw pyrolysis oils, preparation and analysis techniques may also need to differ to target the variation in analytes present in the oils.

One of the most obvious and potentially impacting differences in the preparation of pyrolysis oil samples is the solvent that the oils are solubilized in prior to analysis. Many oils have been fractionated into different solvents prior to separate analysis of the different fractions [5,14,15,20–23]. Typically, there is an initial “wash” of the raw oil with water to remove water-soluble analytes or to separate heavy “pyrolytic lignin” components [15]. Next, the water-insoluble oil residue is usually partially dissolved in dichloromethane, leaving behind a higher-molecular weight solid or tar substance also typically referred to as pyrolytic or high molar mass lignin containing compounds such as lignin and sugar oligomers not typically capable of analysis by GC [3,14,15,22,24]. The dichloromethane-soluble oil is then analyzed by GC for chemical composition. The aqueous layer is washed with an organic solvent such as diethyl ether where the organic fraction is analyzed by GC and the aqueous layer is analyzed by LC techniques [25]. There are other fractionation schemes that have been used to analyze the components of pyrolysis oils that include initial nonpolar solvent washes and other solvents such as ethyl acetate to analyze the bulk of the oil products [15,24].

It has been noted that pyrolysis oils are completely soluble (no phase separation or precipitation) in acetone and can be analyzed by GC upon dissolution in this solvent [26]. However, due to volatility limitations (high molecular weight of some products) and the fact that some products co-elute with the solvent, only 20–40 wt% of the oil can be accounted for by GC analysis [27]. The solubility of pyrolysis oils in various solvents has received little attention aside from the development of fractionation schemes and fuel miscibility studies [5,14,22]. The analysis of oils in solvents in which they are fully miscible and not likely to react is essential for accurate quantitation. Additionally, it is possible that the weight recoveries in solvent fractionation schemes can

elucidate the properties of raw and upgraded pyrolysis oils. Furthermore, different solvents lend different capabilities for analysis, and solubility (or lack of) could affect the accuracy of the analysis by a particularly method, or only provide information on a fraction of the sample. For example, several solvents such as acetone- d_6 [26], DMSO- d_6 [28] and $CDCl_3$ [5,25] have all been used as a solvent for NMR analysis of bio-oils. However, pyrolysis oils may not be completely soluble in chloroform (and hence its deuterated form) [29]. If solids and a separate liquid layer form, the analysis is only representative of the soluble fraction. Similarly, GC analysis of oils in dichloromethane may only be representative of a certain fraction of the oil. It is also possible that some otherwise soluble analytes may be trapped in or mildly soluble in the solids, tars and second liquid layers that form, yielding additional error in the quantitative analysis of these products. There are benefits to fractionating oils prior to analysis though, as fractionation can elucidate mass fractions of particular analyte groups, such as pyrolytic lignin, into different chemical classes [24]. On the other hand, it is possible that fractionation of bio-oils using different solvents (liquid–liquid extraction techniques) is nonselective for particular analytes, functional groups and molecular weights and that additional separation processes (i.e. solid phase extraction, centrifugation, filtering, etc.) may be necessary to separate oils into different chemical fractions.

The goal of this study was to observe the solubility of two different catalytic fast pyrolysis oils in various solvents and in simple solvent fractionation schemes, in order to verify standard solvents for particular analytical methods. Experiments were performed to try to elucidate the relationship between the properties and compositions of these oils with their solvent fractionation profiles. The selective (or nonselective) fractionation of particular CFP oil components into different solvents was also explored. Since most analytical studies have focused on raw pyrolysis oil and hydrotreated oil, the data reported herein also adds fundamental information about the analysis of catalytic fast pyrolysis oil that is needed in current literature. This study also shows how the differences in catalytic fast pyrolysis oil and raw pyrolysis oil compositions may require both different methods of sample preparation as well as different analytical methods.

2. Experimental methods

2.1. Fast pyrolysis

The pyrolysis oils used in this study were produced at the National Renewable Energy Laboratory (NREL) [33]. Briefly, the oils were generated using a fluidized bed reactor where pyrolysis of ground loblolly pine was performed at 500 °C and vapors were upgraded in a separate bubbling-bed catalytic upgrader at two different temperatures, 500 °C for “CFP oil 1” and 600 °C for “CFP oil 2.” “Raw oil” was obtained using the same conditions as CFP oil 1 without the catalyst for comparison. Vapor phase upgrading of the raw pyrolysis vapors was achieved using HZSM-5 SAR 30 (405 m²/g) catalyst from Zeolyst and the final bio-mass/catalyst (mass/mass) ratio used was 1.4/1. The *ex situ* catalytic fast pyrolysis vapors were condensed in a condensation train and the liquids were combined and allowed to separate into three layers: a top organic oil, middle aqueous layer and bottom organic oil (Fig. 1). The three different phases were separated for analysis and characterization (i.e. GC, elemental analysis, water content, total acid number, etc.). The raw pyrolysis oil liquid product was relatively homogenous. This manuscript focuses on the solubility and fractionation of the bottom oil fraction (the most abundant fraction of organic products based on yield as discussed in Section 3.1) of two CFP oils in comparison to raw pyrolysis oil.

2.2. Solvent miscibility

Various solvents were selected to analyze the raw and bottom CFP oils; Table 1 shows the properties of the solvents used in this study to

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