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Research paper

Catalytic hydroprocessing of fast pyrolysis oils: Impact of biomass feedstock on process efficiency

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ABSTRACT

We report here on an experimental study to produce refinery-ready fuel blendstocks via catalytic hydrodeoxygenation (upgrading) of pyrolysis oil using several biomass feedstocks and various blends. Blends were tested along with the pure materials to determine the effect of blending on product yields and qualities. Within experimental error, oil yields from fast pyrolysis and upgrading are shown to be linear functions of the blend components. Switchgrass exhibited lower fast pyrolysis and upgrading yields than the woody samples, which included clean pine, oriented strand board (OSB), and a mix of piñon and juniper (PJ). The notable exception was PJ, for which the poor upgrading yield of 18% was likely associated with the very high viscosity of the PJ fast pyrolysis oil (947 cp). The highest fast pyrolysis yield (54% dry basis) was obtained from clean pine, while the highest upgrading yield (50%) was obtained from a blend of 80% clean pine and 20% OSB (CP_8OSB_2). For switchgrass, reducing the fast pyrolysis temperature to 450 °C resulted in a significant increase to the pyrolysis oil yield and reduced hydrogen consumption during hydrotreating, but did not directly affect the hydrotreating oil yield. The water content of fast pyrolysis oils was also observed to increase linearly with the summed content of potassium and sodium, ranging from 21% for clean pine to 37% for switchgrass. Multiple linear regression models demonstrate that fast pyrolysis is strongly dependent upon the contents of lignin and volatile matter as well as the sum of potassium and sodium.

1. Introduction

The production of renewable motor fuels from lignocellulosic biomass is an attractive alternative to petroleum-based fuels, and remains a key part of the U.S. strategy to ease dependence on imported oil and reduce greenhouse gas emissions [1]. However, for this strategy to be both environmentally and economically feasible, it is important that the development of conversion technologies and biomass resources be coordinated so that the cost-competitive production of biofuels is compatible with the use of sustainable, low-cost, and diverse feedstocks [2,3]. The 2016 Billion Ton Update provides a comprehensive survey of U.S. biomass resource potential, including price and supply curves for various biomass types [4]. While this report affirms the annual availability of a billion tons of biomass that could potentially be converted to motor fuel, the question of feedstock quality is not specifically addressed. To complement the 2016 Billion Ton Update there is a considerable need to understand how different biomass types perform in different conversion processes, including impacts to operations, process efficiency, product quality, and potential waste streams.

One potential thermochemical route to convert biomass to motor fuels is via fast pyrolysis, using rapid heating to moderate temperatures (roughly 500 °C), without oxygen, to convert biomass into solid (char), gas, and liquid (bio-oil) products. The liquids contain upwards of 75% of the starting biomass energy content, but have several undesirable properties that limit their direct use downstream, including instability, low heating value, high viscosity, and high acidity [5]. These properties generally result from a high proportion of oxygenated compounds of varying chemical functionality that need to be removed from the oil. The most common method employed is catalytic hydrodeoxygenation at elevated pressures [6], which generates a hydrocarbon liquid

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suitable for co-processing in a petroleum refinery or blending into finished fuel [7]. The literature contains numerous studies that have investigated the pyrolysis behavior of various feedstocks [8], and some have examined the effect of bio-oil characteristics on hydrotreating [9,10]. While much progress has been made in recent years, there are still large gaps to close in making this route to biofuels cost-competitive. These are primarily due to the complex chemical and physical nature of the oil, which eludes comprehensive characterization, and the closely-related development of robust hydrotreating catalysts, as pointed out by Wang et al. [11]. Fahmi et al. have reported that as the lignin content in the feedstock increases, the organic liquid yield from fast pyrolysis also increases [12]. Other studies have shown an inverse relationship between the ash content and bio-oil yields [13–15]. In addition to product yields, the amount and speciation of inorganic compounds present in the feedstock can affect the bio-oil composition, as higher mineral content leads to higher levels of low molecular weight compounds such as formic acid, glycoaldehyde, and acetol, while decreasing anhydro-sugars like levoglucosan [16]. The pyrolysis step, however, is only one unit operation in the process to produce finished fuel blendstocks, as the bio-oil still must be upgraded via hydrotreatment. Many of the bio-oil contaminants that result in lower hydrotreater yields can be traced back to the feedstock, such as residual solids (char), alkali metals, and high water content in the bio-oil [17]. Hence, in order to fully understand the effect feedstocks have on the yield and quality of finished fuel blendstocks, the integrated pathway must be studied rather than individual unit operations. A recent study by Zacher et al. examined the performance of pine beetle-killed trees and "hog fuel" (mix of woody residues) providing important data for two low-cost resources [18]. Still, as the vast majority of past work has focused on processing clean woody materials, it is difficult to assess, based on the literature, how or why feedstock type or, more specifically, the pyrolysis oil derived from it, affects the outcome of the hydrotreating process.

The impact of feedstock characteristics on thermochemical processing to advanced hydrocarbon biofuels has become a focal point of both academic and U.S. Department of Energy research efforts. Key to the research efforts underway is the ability to simultaneously achieve DOE's feedstock cost, quality, and volume targets, while also achieving conversion cost targets that have been established as benchmarks needed for biofuels to be competitive with petroleum fuels. To this end, Idaho National Laboratory (INL), Pacific National Laboratory (PNNL), and the National Renewable Energy Laboratory (NREL) are partnering to understand the field-to-fuel implications of using different feedstocks in thermal conversion processes. Recently, we reported results from an integrated fast pyrolysis-hydrotreating study for several commercially-relevant feedstocks [19]. This work showed that feedstock choice indeed impacted multiple conversion metrics, including bio-oil yield and composition, hydrotreating yield, H_2 consumption, selectivity to fuel products, and biomass carbon-to-fuel efficiency. Follow-on projections from technoeconomic analyses confirmed that overall conversion costs vary significantly with feedstock, indicating an approximate 40% increase in the cost to convert switchgrass to fuel compared to the base case of clean pine [20]. We report here on these and additional conversion tests and analyses that relate fast pyrolysis and hydrotreating performance to physical and bulk chemical properties of the inputs for each process step, i.e. raw feedstock and pyrolysis oil. The overall processing efficiency as a function of feedstock was examined on the basis of mass, carbon, and chemical energy of the inputs and products.

2. Materials and methods

2.1. Feedstock selection and characterization

The feedstocks for these experiments, shown in Table 1, were acquired and prepared by INL and were chosen to represent significant resources identified in the Billion Ton Update [4]. Feedstocks were included that are available in sufficient quantity to be impactful (~50 million tons/year combined) and that could potentially be blended to meet DOE's cost target for delivered material of $80/dry ton. Oriented strand board (OSB) was chosen to represent the wood-based fraction of construction and demolition waste. Von Holle et al. has reported that piñon-juniper has an unusually high carbon conversion yield of nearly 35% in catalytic fast pyrolysis and that the resulting crude oil had a low oxygen content of approximately 11% [21]. A similar piñon-juniper was included in the present study for comparison. All feedstocks were ground to less than 2 mm. Feedstock characterization included compositional, proximate, ultimate, and elemental ash analyses as described previously [19]. Details of the analytical methods used can be found in the Supplemental Information.

2.2. Fast pyrolysis processing and product characterization

Pyrolysis oils were produced using a 5 cm (2 in.) fluidized bed reactor system (2FBR), which has been described previously [19]. A schematic can be found in the Supplemental Information (see Figure S-1). Briefly, biomass was fed at a rate of 420 g/h by an auger into the 2FBR, which was operated at 500 °C, with the goal of generating 1 L of pyrolysis oil from each feedstock. Char exiting the 2FBR was removed by a cyclone and remaining fines were removed using a hot, in-line vapor filter (2 μm pleated, 316-SS screen). The process lines, cyclone, and filter were heat traced and maintained at approximately 400 °C. The residence time of pyrolysis vapors in the 2FBR system before the condensation train was approximately 2 s. Vapors were condensed in a three-stage condensation train; an air-cooled condenser, followed by an electrostatic precipitator and a dry ice condenser. The total volume of non-condensable gases was measured with a dry test meter before being analyzed by NDIR, GC, and TCD to measure H_2, CH_4, CO, CO_2, and C_2/C_3 hydrocarbons.

A number of techniques were used to analyze the liquid and solid products from the 2FBR. The pyrolysis oils and chars were characterized using proximate, ultimate, and elemental ash analysis. Additional measurements performed on the oils included water content, viscosity, density, acid content, carbonyl content, and calorimetry. Except for carbonyl content, detailed descriptions of the analytical methods have been described previously [19] and are summarized in the Supplemental Information. Carbonyl content was determined by automated titration based on a method originally proposed by Faix [22]. Approximately 0.1 g of oil was dissolved in DSMO (dimethyl sulfoxide) and reacted with a standard mixture of hydroxyl amine hydrochloride:TEA (triethanol amine) for 2 h at 80 °C. The reaction of carbonyl groups in the oil consumed some of the hydroxyl amine and the TEA reacted with the liberated hydrogen chloride. The excess TEA was then back-titrated with standardized hydrochloric acid. Each oil sample was prepared and analyzed in triplicate.

2.3. Pyrolysis oil hydroprocessing and product characterization

The whole pyrolysis oils produced in the 2FBR were upgraded using a two-stage hydrotreater to produce a refinery-ready fuel. A detailed description of the hydrotreating system is given elsewhere [19] and a process flow diagram can be found in the Supplemental Information (Figure S-2). Briefly, the whole oils were introduced by