



Characterization of fast-pyrolysis bio-oil distillation residues and their potential applications



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ABSTRACT

A typical petroleum refinery makes use of vacuum gas oil by cracking the large molecular weight compounds into light fuel hydrocarbons. For various types of fast pyrolysis bio-oil, successful analogous methods for processing heavy fractions could expedite integration into a petroleum refinery for fuel production. This paper investigated the applicability of bio-oil distillation residues (i.e., 'bottoms') toward end-use and/or post-processing through the use of various physical and chemical characterization methods, including FTIR, NMR and their decomposition in a micropyrolyzer (Py-GC-MS). We compared distillate bottoms from both the recently developed tail-gas reactive pyrolysis (TGRP) and traditional pyrolysis bio-oils, emanating from switchgrass and horse manure feedstocks. Based on the FTIR and NMR measurements, we found the traditional bio-oil bottoms to contain more reactive functional groups, whereas TGRP bottoms are highly aromatic and exhibit a lack of functional groups. Manure-based bottoms consistently contained more aliphatic carbons than those of switchgrass origin. However, irrespective of the origin of the feedstock, all bottoms samples possessed high HHVs making them suitable for solid fuel application, such as direct combustion (30 MJ/kg for traditional bio-oil bottoms; 37 MJ/kg for TGRP bottoms). A preliminary evaluation using Py-GC-MS to test their suitability for use in refinery cracking processes revealed that the TGRP-based bottoms all produced significant yields of pyrolyzate (20–50%), with nearly all detected compounds comprising alkyl benzenes and alkyl phenols. However, the manure-based TGRP bottoms produced a higher proportion of C₈–C₁₈ paraffin compounds.

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1. Introduction

While biofuels technological research continues to progress toward development of fungible fuels, a parallel synthesis and/or use of biorefinery co-products are needed to enhance their economic viability. For example, fast pyrolysis of biomass yields a solid carbonaceous solid (biochar) in addition to the liquid organic product. While biochar is normally undesired for fuel, it was shown to enhance carbon sequestration and mineral enrichment within plant soil [1,2]. As a result, biochar demand has steadily risen over the past few years [3,4]. It has been shown that bio-oil produced from tail-gas reactive pyrolysis (TGRP) [5,6] has potential for direct isolation of fuel-grade compounds and petrochemically-relevant coproducts, such as BTEX (benzene, toluene, ethylbenzene, xylenes) and phenols. The TGRP process recycles a portion of the produced non-condensable gases back into the pyrolysis reac-

tor, such that under certain conditions, the reactor atmosphere enhances bio-oil deoxygenation. Owing to the predominance of thermally stable chemical groups, TGRP oil distills with high yields of dry organic non-acidic products (~60–65%) and significantly less residual bottoms, analogous to heavy vacuum gas oil (HVGO) or vacuum residuum. The 65% yield is a significantly better performance than when traditional bio-oil is distilled (<20% dry organic yield), where excessive repolymerization of the pyrolytic lignin occurs [7,8], resulting in more than 40 wt% of the bio-oil left as bottoms. In both cases, a significant residuum fraction necessitates downstream fractionation or conversion into lighter compounds.

The chemical and physical characterization of these distillation residues could expose the pertinent properties that play a crucial role in their potential end use. The heaviest compounds within unmodified bio-oil, regardless of separation method, are likely to be chemically similar to bottoms remaining after bio-oil distillation. Despite the chemical similarities, utilization of these heavy fractions has predominantly focused on pyrolytic lignin [9,10]. Several researchers have illustrated how the unique chemistry of

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pyrolytic lignin can be exploited for use in composite applications [9,11,12]. The hydroxyl group can cross-link with carbonyls present to increase molecular weight, or they can be functionalized to provide enhanced reactivities [13]. Another application is found in asphalt [14], wherein said oligomers and pyrolytic lignin are blended with binders to yield a material suitable for pavement and roofing applications. Furthermore, the pyrolytic lignin fraction could undergo further upgrading into smaller molecular weight components. One upgrading technique involves the use of catalysts for depolymerization [15,16]. Another method diverts the heaviest distillate fraction of bio-oil into a fluidized catalytic cracking (FCC) reactor [17] to reduce molecular weight. Refineries and pyrolysis investigators are currently examining co-processing of whole bio-oil with petroleum FCC feed [18,19,20], which could increase fuel production and eliminate the need for pyrolysis-based HVGO. Since lignin is relatively hydrogen-deficient compared to the petroleum resin fractions, the FCC method may require the use of external hydrogen for cracking (i.e., hydrocracking) [21]. However, the molecular structure of distillate bottoms may be conducive to simple fragmentation into one-ring aromatic structures, which are more valuable for fuel purposes. This paper investigates the potential end-use applications of bio-oil distillate bottoms, especially cracking reactions, as they relate to the methods of characterization used.

2. Materials and methods

2.1. Fast pyrolysis of biomass

Prior to fast-pyrolysis experiments, all feedstocks were ground and dried. Switchgrass (abbr. SwG) feedstock was provided by the McDonnell Farm (East Greenville, PA, USA) and equine manure (Manu) by Morrisville State College Equine Center (Morrisville, PA, USA). Fast-pyrolysis of feedstock was carried out in the ERRC fluidized bed fast pyrolysis system, as described previously [5]. Briefly, 2 kg/h of feedstock is fed through a fluidized sand bed reactor under 500 °C N₂ (Fig. 1a). The resulting vapors then pass through a cyclone which separates out char particulates. Liquid phases are then condensed from the vapor by four condensers in series. Oil precipitates from the non-condensable gases (NCGs) by two electrostatic precipitators (ESPs) in series. All experiments used the oil obtained from the ESPs. For tail-gas recycle experiments, a fraction of the non-condensable gas stream was mixed with the N₂ stream and recycled into the fluidized bed, using a preheater and gas blower. The pyrolysis system recycled the tail gas in the range of 50–70%.

2.2. Bio-oil distillation

Bio-oil samples were distilled using either a fractionating column or a short-path distilling head, as described in recent work [6]. Briefly, 20, 50, or 100 g of bio-oil were heated in a round-bottomed flask connected to a distillation apparatus. Vapors were condensed and collected until the bottoms temperature reached 350 °C. Then, vacuum was applied and more vapors were condensed and collected. After removing the vacuum and turning off the heating mantle, the flask was allowed to cool. The hard glassy bottoms residue was chipped, scraped, and collected from the flask and crushed into a granular powder with a mortar and pestle. Nomenclature: SwG-TGRP or Manu-TGRP = bottoms from switchgrass or manure TGRP bio-oils, respectively; SwG-reg or Manu-reg = bottoms from switchgrass or manure regular bio-oils, respectively.

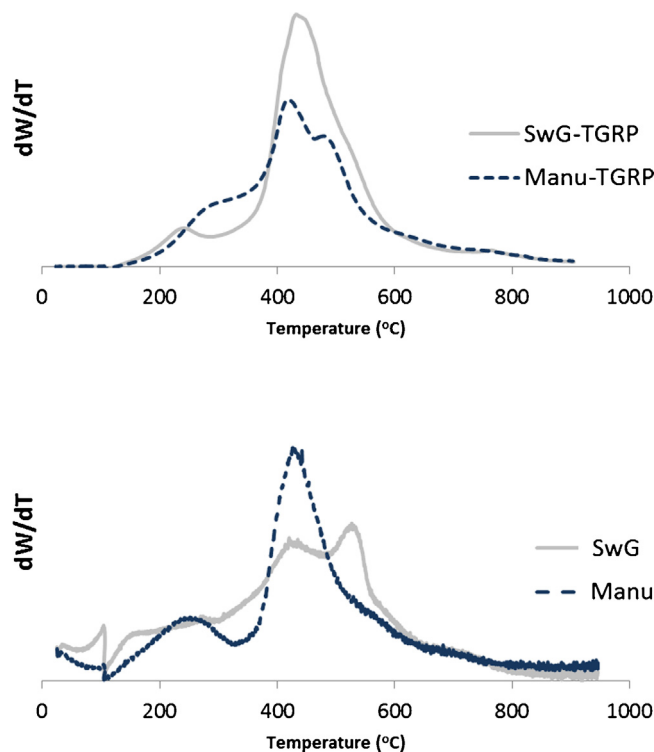


Fig. 1. TGA differential weight loss curves for the four distillate bottoms samples.

2.3. Characterization

Elemental analysis (CHN) by combustion was carried out using a Thermo EA1112CHNS analyzer. Oxygen content was determined by difference. Ash content was determined by heating the sample in a crucible to 750–850 °C (ambient air) overnight. The mass remaining was weighed to be the ash content. Thermogravimetric analysis (TGA) was performed using a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE). Between 15 and 20 mg of sample was heated at either 1 or 10 °C/min until a temperature of 950 °C was attained. The Py-GC-MS experiments were conducted using the Pyroprobe 5250-T (CDS Analytical) directly connected to an Agilent 6890N gas chromatograph (GC) which is equipped with an Agilent 5973 mass spectrometer detector. Each experiment was conducted with 100–300 mg of bottoms sample. The GC separation of pyrolysis vapors was done with a 60 m × 0.25 mm DB-1701 column (0.25 μm film thickness) with He carrier gas (1 mL/min). The GC inlet was 250 °C and a split ratio of 90:1 was used. The oven was programmed to start at 45 °C, hold for 4 min and then ramp at 3 °C/min to a final temperature of 280 °C where it was held for 20 min. Peak identification was done using the NIST mass spectrum library. Some of the identified phenolics and aromatic hydrocarbons were quantified. The quantification was done by the external standard method. Standards were prepared as dilute solutions of the analytes in acetone at four concentrations. Each standard was injected (1 μL) into the system, and four point linear calibration curves with $R^2 \geq 0.98$ based on three characteristic mass ion signals of each compound were generated. Precision of at least 0.1 μg, (~0.05% yield from pyrolysis) differences was achieved. For mass yield experiments, 1.0 mg samples were used, samples were pyrolyzed at the desired temperature for 20 s (filament heating rate of 1000 °C/s), and total pyrolyzate yields were calculated by difference in mass before and after micro-pyrolysis, accounting for losses of quartz wool packing. ¹H and ¹³C NMR spectroscopy was conducted with a Varian 400 MHz spectrometer (Agilent Technologies, Santa Clara, CA). FTIR spectra of solid samples were obtained using a Nicolet Nexus 670

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