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# Co-cracking of bio-oil distillate bottoms with vacuum gas oil for enhanced production of light compounds☆

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ABSTRACT

Seamless co-processing of pyrolysis bio-oil within existing petroleum refineries is the most synergistic and economic way to improve biorefinery output. Coprocessing bio-oil with vacuum gas oil (VGO) is one logical pathway. Bio-oil has a viscosity and molecular weight range similar to that of VGO, and the hydrogen-rich nature of VGO can chemically complement the bio-oil hydrogen deficiency. Distillation of biomass pyrolysis oils produces solid residues with a significant fraction of fixed carbon and heavy volatiles. Maximization of yields of light compounds like olefins and gasoline-range aromatics are crucial for both attainment of desired product output levels as well as to follow methods that mimic petroleum-based methods and chemistries. Herein we discuss a systematic study on the additive coprocessing of specific bio-oil distillation bottoms with VGO. Tail-gas reactive pyrolysis (TGRP) bio-oils from spirulina, switchgrass, and guayule biomasses were distilled, and their bottoms were subject to analytical experiments in mixtures with VGO over different zeolite catalysts (no catalyst, HZSM-5, Y-zeolite). Switchgrass-based bottoms exhibit greater hydrogen deficiency and higher oxygen content compared with that of spirulina or guayule. Switchgrass-based bottoms, with or without VGO, produced more aromatics and less olefins and alkanes, compared with spirulina or guayule bottoms. When compared across different mixing ratios, thermal cracking of a 10:1 guayule/VGO mixture resulted in higher aromatics yields than even the VGO by itself. Addition of more VGO up to a 1:1 ratio of VGO/switchgrass bottoms nearly tripled the production of BTEX compounds. For hydrogen-rich bottoms spirulina and guayule, LPG-range olefins yields increased nearly 50% for 1:1 VGO/bottoms blends, compared with theoretical yields.

## 1. Introduction

Production of renewable alternatives to liquid fuels and/or chemicals will require flexible techniques that adapt to economic circumstance. Both biochemical and thermochemical methods [1,2,3] can convert biomass to liquid fuel intermediates for eventual refining into finished products, but thermochemical methods may offer extra economic advantages [4]. As an example, fast pyrolysis can produce biofuels and renewable chemicals potentially on commercial scales, via integration with existing petroleum refinery infrastructure [5]. Furthermore, several petrochemical products cannot be obtained by solely biochemical means. One example is the solid residues from petroleum distillation which are normally processed into asphalt and/or coke [6,7]. For refinery integration to realistically work, methods for processing bio-oil residues should then be analogous to methods for petroleum residues. Fluid catalytic cracking (FCC) [8] and delayed coking [6] aid in producing greater amounts of light hydrocarbon compounds from solid resides, which subsequently increases profit. Since delayed coking produces about 8–10% yields of gases [9], yield increases by as little as 1–5% are relatively significant and can boost profits. This is due to the large scale of processing for oils.

In the past, co-processing of petroleum with highly oxygenated bio-oils has met challenges [10]. Recent advances in pyrolysis technologies [11,12] have enabled production of bio-oils with low oxygen, making them more amenable to post-pyrolysis refining techniques like distillation [13]. However, the challenges behind processing pyrolysis oil distillation bottoms are identical to those of processing light bio-oil fractions. These challenges originate from the stark differences in chemical characteristics from petroleum: 1) pyrolysis bio-oils are primarily hydrogen-deficient aromatics, whereas petroleum primarily consists of hydrogen-rich naphtha and paraffins. 2) bio-oil bottoms, much like bio-oil, contain significant concentrations of heteroatoms O and/or N. Even though distillate bottoms from advanced pyrolysis techniques [14] (e.g. catalytic, TGRP) primarily contain polyaromatic hydrocarbons (PAHs),

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some oxygenated functional groups remain, making its introduction into the existing petroleum flow streams incompatible. Hence, strategies for producing useful compounds from heavy pyrolysis bottoms likely will differ significantly from those of petroleum bottoms.

One method of recent interest revolves around co-processing heavy petroleum bottoms like vacuum gas oil (VGO) with bio-oil [15,16,17,18,19]. Bio-oil has a viscosity and molecular weight range similar to that of VGO, and the hydrogen-rich nature of VGO can chemically complement the bio-oil hydrogen deficiency. Hence, the appropriate process conditions and catalyst can facilitate synergistic reactions between the two streams which enhances production of useful compounds. Some investigators [18,10] have tested the concept of co-processing pyrolysis oil with VGO in pilot-scale tests, though these tests have their limitations. For some, low dilutions of bio-oil were used, presumably due to lack of miscibility and an acceleration of chemical reactions brought on by bio-oil. However, bio-oil distillation mixtures with VGO have not been tested. Bio-oil distillation [13,20] is a relatively new outlet that is useful for advanced pyrolysis oils. Distillation isolates solid bottoms and separates water away from light organics without compromising organic yields. Little, if anything, has been accomplished with regards to heavy bio-oil bottoms coprocessing; applications are limited to high molecular-weight products like asphalt [21], composite reinforcement [22,23], and calcined coke [24]. The bottoms are generally characterized as being highly hydrogen-deficient polyaromatic strucutres, with some remaining oxygen (or nitrogen) functionality. This makes recovery of additional volatile organics from the bottoms difficult. However, co-processing with a hydrogen rich material may increase potential for conversion of this recalcitrant carbon to increase the overall recovery of volatile compounds from an advanced biomass pyrolysis process.

While all of the volatile fractions in TGRP bio-oil can undergo HDO with high yields, only a portion of the distillate bottoms, to date, has been converted into a final co-product. Isolation of the heavy volatiles within distillate bottoms is too heavy to distill without interrupting formation of calcined coke. Furthermore, some of the fixed carbon within the bottoms is capable of thermal and/or catalytic breakdown into light compounds. Since distillation of bio-oil is a relatively new area, cracking of heavy bio-oil bottoms to increase yields of light compounds has been studied to an even lesser degree. In this preliminary study, we detail the thermal and catalytic high temperature cracking of mixtures of bio-oil distillate bottoms, with the purpose of enhancing yields of useful volatile compounds including combustible gases, olefins and aromatic hydrocarbons and for guiding larger-scale experiments.

## 2. Experimental

### 2.1. Pyrolysis oil distillation

TGRP bio-oils from guayule bagasse, spirulina, and switchgrass biomasses were distilled according to previous protocols [13]. Briefly, 100 g of pyrolysis oil were heated in a round-bottom flask attached to a distillation apparatus. Vapors were collected through cold water condensation until the bottom temperature reached 350 °C. Then, vacuum was applied to collect residual vapors. After removing vacuum and turning off the heating mantle, the round-bottom flask was cooled down to room temperature over several hours. Solid bottoms were collected from the flask and crushed into powder with mortar and pestle. Bottoms of guayule bagasse, spirulina, and switchgrass were abbreviated GB, SP, and SwG, respectively.

### 2.2. Py-GC/MS experiments

Py-GC/MS experiments were conducted using a double shot micropyrolyzer (model 2020iS, Frontier Laboratory, Japan) connected to a GC–MS. Approximately 0.5 mg of various mixtures of VGO and distillation bottoms (10:1, 5:1, 2:1, and 1:1) were placed in a sample cup and thermally cracked at three temperatures (750 °C, 850 °C, and 950 °C). The resulting vapors as well as the non-condensable gases (carbon oxides, alkanes and olefins) were quantified by GC–MS. For catalytic experiments, ZSM-5 ($SiO_2/Al_2O_3$ = 23; 425 $m^2/g$ BET surface area) and Y-type ($SiO_2/Al_2O_3$ = 5.1; 925 $m^2/g$) zeolites were purchased from Zeolyst (Conshohocken, PA) and were added in a 1:2 sample:catalyst mass ratio post-activation. Catalysts were activated by heat treatment in a muffle furnace at 500 °C for 4 h, to produce HZSM-5.

The column used for chromatographic separation of condensables was a RTX-1701 (60 m length × 0.25 mm ID × 0.25 μm film thickness). The GC oven was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C, and then hold for 20 min. The injector was maintained at 250 °C and a split ratio of 30:1 was used. For the analysis of non-condensable gases, identical experiments were performed with a different column and GC method. A split ratio of 100 and a CP-PoraBOND Q, 25 m × 0.25 mm fused silica capillary column was used (Varian, Palo Alto, CA). The oven for the GC column was set at 35 °C for 3 min followed by a ramp rate of 5 °C/min up to 150 °C then 10 °C/min to 250 °C and held for 45 min for a total run time of 81 min. Quantitative analysis of the yield of individual chemical products was done by the external standard method, using pure samples of known concentrations to generate calibration curves, according to previously-published methods [25]. A four-point calibration curve method was used. MS detection was carried out under electron ionization conditions in full scan in the *m/z* interval 14–350 with a threshold at 1000.

### 2.3. Characterization

Elemental analysis was performed using a Thermo EA1112 CHNS/O analyzer. Oxygen content was determined by difference. Thermogravimetric analysis (TGA) was performed using a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE). Approximately 15 mg of sample was heated under nitrogen at 10 °C/min until the desired temperature of 1000 °C was attained. Solution-state NMR spectra were recorded at 14.1 T on an Agilent VNMRS DD2 NMR Spectrometer, using a 5 mm OneNMR probe, equipped with z-axis pulsed field gradients. All bottom samples were prepared by adding 600 μL of $d_6$-dimethylsulfoxide to the material and allowing it to dissolve overnight. The dissolved supernatant was then transferred to an NMR tube. The VGO sample was prepared by dissolving ~50 μL of sample in 600 μL of d-chloroform. Tetramethylsilane (0.05% v/v) was used as an internal chemical shift reference for all $^1$H spectra, whereas the solvent peak was used for the $^{13}$C spectra. The $^1$H spectra were acquired with a 45° pulse angle, a 20 s relaxation delay and a spectral-width of 12 ppm using (centered at 5.5 ppm) using 32 k data points. All $^{13}$C spectra were acquired at 40° C, using a spectral-width of 250 ppm (centered at 110 ppm) and were acquired using: a 45° pulse angle, 6 s relaxation delay, 0.87 s acquisition time, 64 k data points and inverse-gated proton-decoupling to avoid NOE enhancement of $^{13}$C signal from attached protons. The number of transients averaged for each spectrum was 65056. Based on previous studies, all detectable $^{13}$C signals are expected to be relaxed under these experimental conditions.

## 3. Results and discussion

### 3.1. Distillate bottoms characterization

The chemical characterization of the distillate bottoms guides our understanding of how the pyrolysis experiments relate to the starting material. In that light, we used $^1$H NMR (Table 1) spectrometry to elucidate differences in structural configurations. In contrast to VGO, distillate bottoms from pyrolysis oils contain larger amounts of aromatics and oxygenated/nitrogenated compounds and fewer alkanes. Guayule bagasse (GB) and spirulina (SP) bio-oils contain various aliphatic compounds [26,27], which reflect also in the distillate bottoms