

Co-hydroprocessing HTL Biocrude from Waste Biomass with Bitumen-Derived Vacuum Gas Oil

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ABSTRACT: In this study, we investigate the feasibility of co-processing biocrude in petroleum vacuum gas oil (VGO) hydroprocessing units. The biogenic component of the feed was biocrude produced by hydrothermal liquefaction of woody biomass, while VGO from oil sand bitumen was selected as the hydrocarbon feed. To improve its processability, the biocrude sample was distilled to remove high boiling components prior to testing. Systematic experiments were conducted in a continuous hydroprocessing pilot unit at co-processing ratios of up to 15 vol % biocrude and reaction temperatures of 350–380 °C, including baseline tests with pure VGO, to understand process impacts. The operating range where there was a minimal effect on hydrodesulfurization and hydrodenitrogenation activity levels over the baseline was at co-processing ratios below 10 vol % biocrude and temperatures of 370 °C and above. Monitoring of catalyst stability through check-back experiments with pure VGO revealed visible deactivation trends at co-processing ratios above 10 vol % biocrude. Radiocarbon analysis allowed the establishment of the fate of biogenic carbon added to the co-processing feed. This study suggests that VGO hydroprocessing units, as normally used at the front of fluid catalytic cracking and hydrocracking units in a refinery, could be a suitable cut-in point for biocrude within a carefully delimited operating window.

1. INTRODUCTION

Transitioning to renewable transportation fuels is becoming a primary strategy to fulfill climate change commitments. In Canada, federal government regulations require that transportation fuels produced in or imported into Canada have a renewable content of at least 5 vol % in gasoline and 2 vol % in diesel fuel.¹ The current practice to meet this requisite is blending ethanol from corn into petroleum gasoline and biodiesel into petroleum diesel. The challenging aspect of this approach is accessing these biofuel blendstocks at a large-enough scale and economically competitive prices. Co-processing biogenic feedstocks with petroleum streams in refinery units is an alternative pathway that could help addressing this problem by leveraging existing infrastructure and utilities in a refinery.²

There have been studies in the literature documenting the testing of biogenic feedstocks for their suitability for co-processing. Vegetable oils, animal fats, and pyrolysis bio-oils have been examined using hydroprocessing and fluid catalytic cracking (FCC) technologies at the laboratory and pilot plant scales.^{2–5} There is also scattered evidence that demonstration-scale and commercial trials have been taking place.^{6–8} Vegetable oils, such as canola oil, appear to be a straightforward option in terms of their processability and miscibility with petroleum feedstocks.^{9–11} However, their limited availability in certain regions of the world, along with the controversy around the use of food supplies for fuel production, has shifted interests toward biogenic feedstocks originating from thermochemical conversion of waste biomass sources, such as forestry residues and agricultural wastes.

Bio-oils produced by fast pyrolysis of woody biomass are representative of this category. Fast pyrolysis is considered a mature technology, whereas refining of its liquid bio-oil product is still a developing technology area.¹² Having typically up to 40 wt % oxygen and being chemically unstable and

immiscible in petroleum,¹³ pyrolysis bio-oils impose serious challenges for their upgrading and/or co-processing into transportation fuels. Catalytic hydrodeoxygenation (HDO), a technology adopted from petroleum hydroprocessing, has been proven to convert bio-oil into hydrocarbons but shows limitations related to catalyst stability, hydrogen consumption, and reactor fouling, according to published studies^{12,14,15} on advances in pyrolysis bio-oil upgrading. Several studies^{16–19} proposed using HDO as a pretreatment step before co-processing, with the goal of stabilizing pyrolysis bio-oil and making it miscible in petroleum and less detrimental to refining catalysts. However, one particular co-processing study,²⁰ in a demonstration-scale FCC unit, has shown that the miscibility problem can be overcome by feeding the bio-oil separately into the reactor without contacting the main feed. Thus, it appears that the miscibility requisite for co-processing of bio-oil is more relevant in conventional experimental setups that are not equipped with separate feed systems.

In view of the challenges faced by pyrolysis bio-oils, there has been increased interest in hydrothermal liquefaction (HTL) bio-oils, very often referred to as biocrudes. HTL biocrudes from woody biomass are distinctive in the sense that they have significantly less oxygen (typically <15 wt %)²¹ than pyrolysis bio-oils and are more thermally stable, making them more amenable for refining. Nevertheless, there is limited experience with processing biocrudes, mostly because HTL technologies have not yet reached commercialization.²² Hoffmann et al.²³ assessed the prospects of co-processing HTL biocrude in a refinery by analyzing the chemical properties of its distillable fractions and concluded that

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HDO pretreatment is required to reduce the impact of oxygenates on refinery units. Ramirez et al.²⁴ reviewed options to process HTL biocrudes, with an emphasis on HDO, distillation, and solvent extraction. In a separate study focusing more on co-processing,²⁵ the same researchers investigated the miscibility problems of HTL biocrude and petroleum resulting from the differences in polarity and concluded that HDO can help improving miscibility to produce a co-processing feed. HDO testing of HTL biocrude^{26,27} confirmed that this approach can reduce oxygen content to a low level and increase the yield of distillable fractions. Mathieu et al.²⁸ evaluated co-processing strategies comprised of distilling raw HTL biocrude to remove heavy fractions, followed by either direct FCC with vacuum gas oil (VGO) or hydrotreating the biocrude distillate first and then subjecting its heavy fraction to FCC with VGO. Direct FCC was found to be feasible at co-processing ratios below 10 wt % biocrude, whereas the hydrotreating pathway gave biogenic gasoline- and diesel-range products along with a deoxygenated gas oil fraction that could be co-processed at ratios above 10 wt % in FCC. Sauvanaud et al.²⁹ demonstrated co-processing of up to 20 wt % distilled HTL biocrude in light gas oil to make a diesel-range product.

As can be seen from the cited literature, there are various potential pathways to co-process HTL biocrudes, and typically, a pretreatment step is required, but the nature of this pretreatment step is not well established. The objective of this study is to investigate the feasibility of co-hydroprocessing HTL biocrude from woody biomass with petroleum, specifically targeting the hydroprocessing units that are used for preparing VGO streams for FCC and hydrocracking. Our hypothesis is that VGO hydroprocessing units can act as a complementary deoxygenation stage for biocrude to produce suitable feedstock for the subsequent refining units. Systematic pilot plant trials were conducted to assess the operational impacts of co-processing biocrude and to establish an operating window that favors its implementation.

2. EXPERIMENTAL SECTION

2.1. Feedstock Selection and Preparation. A straight-run vacuum gas oil (343–524 °C) from Canadian oil sand bitumen was selected as the reference petroleum feedstock based on its miscibility with biocrude. This particular VGO was recognized as a preferable solvent for biocrude owing to its polarity and high aromatic content. This is in line with the compatibility study by Manara et al.,³⁰ proposing aromatic-rich streams, such as light cycle oil (LCO) from FCC and straight-run light VGO, as suitable base feed candidates for co-processing. The starting biogenic component of the feed was a full-range HTL biocrude from woody biomass supplied by Steeper Energy. As pretreatment measures to improve processability and miscibility with hydrocarbons, the full-range biocrude sample was first filtered to remove sediments and then distilled to separate out associated water and heavy material. Biocrude distillation was performed using an ASTM D-1160 vacuum distillation setup with the target cutoff temperature set at 525 °C so that the resulting biocrude distillate was consistent with the VGO in terms of upper boiling point limit. The co-processing feedstocks were prepared by blending the biocrude distillate into the VGO at volume ratios of 5, 10, and 15 vol % biocrude.

2.2. Co-hydroprocessing Tests. Co-processing experiments were conducted in a continuous hydroprocessing pilot unit having a tubular reactor (length = 105 cm and diameter = 0.9 cm). The reactor was set up to run in an upflow mode to maximize wetting of the catalyst bed and manage its thermal stability.³¹ Heat supply to the reactor was controlled by a four-zone electric furnace, combined with a set of thermocouples to measure and control the reactor

temperature profile. The reactor effluent reported to a high-pressure separator (HPS) with a condenser at the top to separate gas and liquid products. Composition of the product gas stream was measured online by a gas chromatograph (GC).

The experimental program was executed using a commercial NiMo/Al₂O₃ catalyst for VGO hydrotreating. Figure 1 shows the

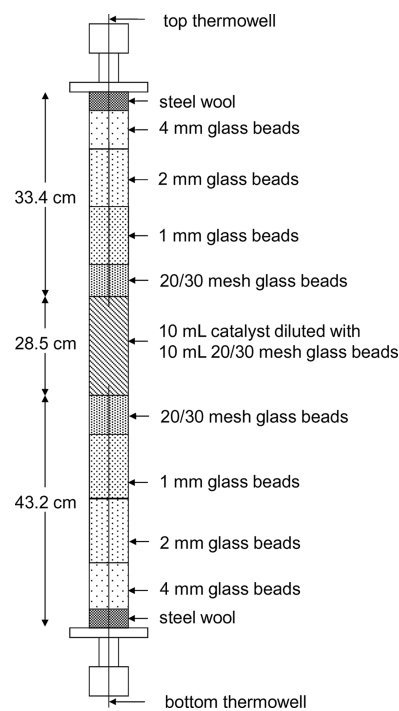


Figure 1. Reactor packing diagram.

reactor packing diagram. The catalytic bed in the middle section of the reactor was made up of 10 mL of commercial-sized catalyst particles (average size, ~2.3 mm), mixed with another 10 mL of 20/30 mesh glass beads as a dilution medium. Catalyst bed dilution is a common practice to reduce wall effects and axial dispersion in experimental reactors.³² The upper and lower sections of the reactor were packed with an inert material of different sizes to facilitate reactant and heat distribution. The two thermowells (0.5 mm outer diameter) housing the thermocouples were inserted through the central axis on each end of the reactor, slightly slipping into the section containing the catalyst bed. The catalyst was activated in situ by liquid-phase sulfiding using light gas oil spiked with 3 wt % dimethyl disulfide (DMDs) and stabilized by processing VGO for 160 h at 360 °C.

The test plan was consisted of four sets of trials, one for each feedstock at different reaction temperatures. The first set of trials was conducted with pure VGO to establish a baseline for the study. Subsequently, the three co-processing feeds (5, 10, and 15 vol % biocrude) were tested one after another. Each set of trials included experiments over the reaction temperature range of 350–380 °C, keeping liquid hourly space velocity (LHSV), pressure, and H₂/oil ratio constant at 1.5 h⁻¹, 6.9 MPa, and 800 NL/L, respectively. Check-back measurements at reference operating conditions (temperature, 360 °C; LHSV, 1.5 h⁻¹; pressure, 6.9 MPa; H₂/oil ratio, 800 NL/L) using pure VGO feed were taken approximately every 200 h to study catalyst stability during co-processing. Mass balance runs lasted between 6 and 24 h, allowing the collection of the sufficient product sample for analysis. The entire experimental campaign was completed over a period of 1420 catalyst h. On average, mass balance closure for the experimental program was 99.1% with a standard deviation of 1.7%.

2.3. Characterization of Feedstock and Products. The bulk properties of the starting VGO and biocrude feedstocks and co-

Table 1. Properties of VGO, Full-Range Biocrude, Biocrude Distillate, and Co-processing Blends

property	VGO	full-range biocrude	biocrude distillate	5 vol % blend	10 vol % blend	15 vol % blend
density at 15.6 °C, g/cm ³	0.9759	1.0536	0.9925	0.9769	0.9780	0.9793
carbon, wt %	84.8	80.0	79.5	84.2	83.6	83.9
hydrogen, wt %	11.1	9.4	10.0	11.1	11.5	11.4
sulfur, wt %	3.6	0.0	0.0	3.4	3.2	3.0
nitrogen, wt %	0.3	0.1	<0.02	0.3	0.3	0.3
oxygen, wt %	0.5	10.5	10.6	1.0	1.4	2.0
SARA analysis						
saturates, wt %	32.9	1.2	2.3	30.3	29.2	29.0
aromatics, wt %	54.1	9.7	16.7	51.1	47.7	47.0
polars, wt %	13.0	44.0	73.7	18.4	22.7	23.2
<i>n</i> -C ₅ insolubles, wt %	0.0	45.0	7.3	0.2	0.4	0.8
Simulated distillation						
IBP, °C	298.0	57.4	57.8	252.8	211.8	150.6
5 wt %, °C	344.0	190.4	158.6	335.8	323.4	302.2
10 wt %, °C	362.4	239.8	199.8	357.2	350.4	341.0
30 wt %, °C	405.2	353.6	283.0	401.0	396.6	391.0
50 wt %, °C	435.2	414.4	348.0	431.2	428.6	425.2
70 wt %, °C	467.0	604.8	377.0	461.4	459.6	456.4
90 wt %, °C	519.4		451.0	506.0	504.8	502.0
95 wt %, °C	568.0		489.0	527.4	526.6	523.2
FBP, °C			702.4	662.6	675.4	636.8

processing feed blends and hydrotreated products were measured using the following standard analytical methods: liquid density at 15.6 °C (ASTM D4052), simulated distillation (SimDis) (ASTM D7169), elemental analysis C/H/N/S (ASTM D5291/D4294), oxygen content by direct determination using an Elementar oxygen analyzer (in-house method), trace nitrogen by chemiluminescence detection (ASTM D4629), and hydrocarbon types by SARA analysis (ASTM D2007).

Selected hydrotreated products were analyzed for biogenic carbon content using radiocarbon analysis (ASTM D6866) and hydrocarbon-type distributions by two-dimensional gas chromatography (GC × GC) with a flame ionization detector (GC × GC-FID). The GC × GC instrument comprised an Agilent 6890 gas chromatograph with a split/splitless injector, a Leco Instruments liquid nitrogen-cooled quad-jet cryogenic modulator, and an Agilent Sievers SCD operating in tandem with an Agilent FID. The columns used for the analyses were: (1) primary column, Agilent VF-5ht (29.5 m × 0.32 mm × 0.1 μm), and (2) secondary column, SGE Analytical Science BPX-50 (1.25 m × 0.1 mm × 0.1 μm). The main oven temperature was initially maintained at 50 °C for 1 min and then increased at a rate of 3 °C/min to 360 °C, where it was held for 1 min. The secondary oven temperature program was set up in a similar manner but offset from the main oven by +10 °C. Method-specific parameters were as follows: inlet temperature, 340 °C; sample injection volume, 0.5 μL; split ratio, 50:1; carrier gas, helium (grade 5.0, Linde); modulator temperature, +45 °C offset from the main oven; modulation period, 6 s. All samples were diluted in dichloromethane (DCM) (1:10) before running the GC × GC analysis.

3. RESULTS AND DISCUSSION

3.1. Feedstock Properties. The bulk physical and chemical properties of the VGO feed, full-range biocrude, biocrude distillate, and three co-processing blends are listed in Table 1. The oil sand-derived VGO that was used as the base feedstock is high in sulfur (3.6 wt %) and nitrogen (0.3 wt %) and, in terms of hydrocarbon types, is predominantly aromatic (54.1 wt %), with a noticeable amount of polar compounds (13.0 wt %) as per SARA analysis. The starting full-range HTL biocrude is denser than water (1.0536 g/cm³) and has 10.5 wt % oxygen. According to SARA analysis, nearly half of the biocrude sample is insoluble in *n*-pentane (45.0 wt %), with

the rest being mostly polar compounds (44.0 wt %), and some aromatics (9.7 wt %) and saturates (1.2 wt %). It is important to acknowledge that these classes are not comparable to their petroleum counterparts since the SARA method is not designed for biocrude analysis. Given that oxygen distribution in biocrude is fairly even over its boiling range,²³ it is likely that these nonpetroleum SARA classes are heavily composed of oxygenated compounds. Speciation by gas chromatography–mass spectrometry (GC–MS) of HTL biocrude distillate fractions boiling up to 350 °C has shown prevalence of ketones, alcohols, and oxygenated aromatics,³³ which concurs with this view.

ASTM D-1160 distillation of the full-range biocrude yielded a 63.4 wt % distillate fraction (IBP–520 °C), with the rest being the 520 °C+ residue (36.5 wt %) and a minor amount of water (0.1 wt %). Note that the actual cutoff temperature that was achieved was slightly below the target value of 525 °C. Distillation yields are reported in Table 2. The corresponding

Table 2. Biocrude Distillation Yields

fraction	ASTM D-1160	SimDis
IBP–343 °C, wt %	26.8	27.8
343–520 °C, wt %	36.6	34.6
520 °C+, wt %	36.5	37.6
water, wt %	0.1	

yields from SimDis, also reported in Table 2, have a good correspondence with the actual distillation values. As shown in Table 1, the resulting biocrude distillate fraction is slightly less dense (0.9925 g/cm³) than water and its oxygen content (10.60 wt %) is virtually the same as the full-range biocrude, suggesting a uniform oxygen distribution. SARA analysis shows a visible increase in the share of polars (from 44.0 to 73.7 wt %) in the distillate, with a significant drop in the *n*-pentane insoluble material, down from 45.0 wt % in the full-range biocrude to 7.3 wt % in the distillate. This shift in SARA

composition has an important effect on biocrude miscibility with petroleum fractions, as discussed below.

The data for the three co-processing feedstock blends (5, 10, and 15 vol %) in Table 1 exhibit an increasing trend in density, oxygen, and polars, proportional to the amount of biocrude distillate added into the blend. The most noticeable changes are in oxygen content, going up from 0.5 wt % in VGO to 1.0–2.0 wt % in the blends and polars, which increase from 13.0 wt % to 18.4–23.2 wt %. The co-processing blends also have an extended boiling profile on the lower end because about 48.0 wt % of the biocrude distillate is a light material boiling below 343 °C. It is also noted that the SimDis instrument is unable to capture the initial boiling point (IBP) of biocrude (~57 °C) in the co-processing blends due to dilution effects.

Finally, we point out that while SARA analysis in its current form cannot give precise answers about the composition of biocrude, it can offer guidance on the processability of biocrude with petroleum streams. More specifically, we found that *n*-pentane insolubles could be used as an indication of biocrude miscibility with hydrocarbons. This was recognized during an attempt to blend the full-range biocrude having 45 wt % *n*-pentane insolubles with VGO, which resulted in the immediate formation of aggregates upon mixing, that rapidly precipitated out of solution (see Figure 2). Removal of a large

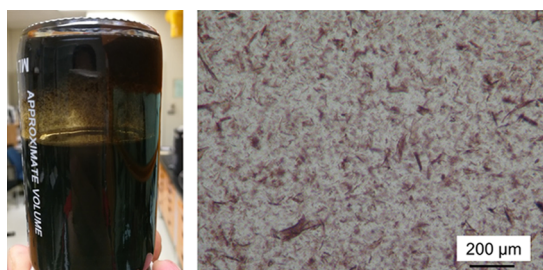


Figure 2. Miscibility behavior of 95 vol % VGO/5 vol % full-range biocrude blend. (Left image) Material deposition was observed when blending the biocrude into VGO in the test bottle. (Right image) Optical microscope image showing the aggregates formed in the blend.

portion of this insoluble material in the distillation step coincided with an improvement in VGO/biocrude miscibility, resulting in stable mixtures at blending ratios of up to 15 vol % biocrude. Considering the cutoff temperature used for distilling the biocrude, it is evident that these unknown compounds contributing to the incompatibility between biocrude and VGO are mostly concentrated in the high boiling fractions of biocrude. Pyrolysis-GC × GC–MS characterization of the HTL biocrude 350 °C+ distillation residue has shown that the pyrolyzed fragments of residue constituents are mostly oxygenated aromatics and some oxygen-free aromatics having up to three condensed rings,³³ which point to highly polar oligomer structures that were not fully broken down during the HTL process. Analogously, characterization studies^{34,35} on pyrolysis bio-oils have proved the presence of various types of oligomeric structures in their high-molecular-weight fractions. Further elucidation of biocrude heavy fractions containing the *n*-pentane insoluble class of SARA is needed due to the role they play in defining and deciding a co-processing strategy. Likewise, there is an opportunity to develop standardized methodologies to measure miscibility of bio-oil/biocrude in petroleum.

3.2. Impact of Co-processing on Catalyst Activity and Stability. Considering that the main purpose of VGO hydrotreating units in a refinery is to produce low-sulfur, low-nitrogen feedstock for FCC and hydrocracking, particular emphasis was placed on the effects of biocrude on these two process parameters. Figures 3 and 4 illustrate the impact of

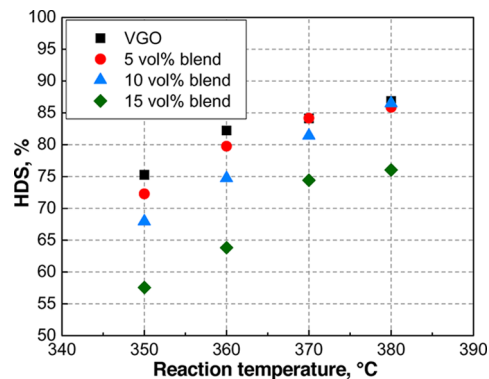


Figure 3. Hydrodesulfurization (HDS) at different temperatures for the base VGO and co-processing blends.

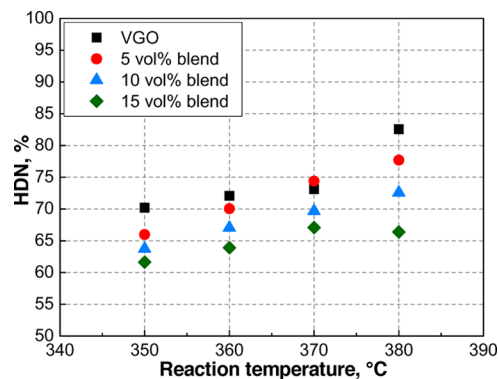


Figure 4. Hydrodenitrogenation (HDN) at different temperatures for the base VGO and co-processing blends.

biocrude co-processing on hydrodesulfurization and hydrodenitrogenation activities over the studied temperature range. It is immediately apparent that HDS and HDN levels for the biocrude blends are below the levels that were achieved with pure VGO. The drop in HDS and HDN activity becomes more visible as more biocrude is added into the VGO feed. For example, for the 15 vol % biocrude blend at 360 °C, HDS decreases by as much as 18.4% and HDN drops by 8.2% with respect to the VGO baseline. This gap in HDS activity, however, virtually disappears for the 5 and 10 vol % biocrude blends at temperatures above 370 °C. In the case of the 15 vol % biocrude blend, an increase in temperature did not shrink the HDS gap. A somewhat similar pattern is observed for HDN up to a temperature of 370 °C. However, at 380 °C, the HDN data diverges from the expected trend.

The diminished HDS and HDN activity levels during the co-processing tests are attributed to inhibitory effects of biocrude components on hydrotreating reactions and to catalyst deactivation. The products of decarbonylation and decarboxylation of oxygenated compounds, which are carbon monoxide (CO) and carbon dioxide (CO₂), respectively, have been reported to be strong inhibitors of hydroprocessing catalysts.^{36–38} As shown in Table 3, CO and CO₂ were in fact

Table 3. GC Analysis of Gas Products

compound	VGO				5 vol % blend			10 vol % blend				15 vol % blend				
	350	360	370	380	350	360	370	380	350	360	370	380	350	360	370	380
temperature, °C	350	360	370	380	350	360	370	380	350	360	370	380	350	360	370	380
CH ₄ , mol %	0.29	0.37	0.54	0.87	0.38	0.52	0.67	0.93	0.44	0.61	0.77	1.06	0.51	0.65	0.89	0.86
CO, mol %	0.00	0.21	0.20	0.23	0.35	0.39	0.39	0.39	0.45	0.50	0.53	0.62	0.56	0.63	0.72	0.58
CO ₂ , mol %	0.05	0.04	0.05	0.05	0.07	0.06	0.06	0.06	0.09	0.09	0.09	0.08	0.13	0.13	0.13	0.16

detected in the gas products of the co-processing runs in higher concentrations (0.35–0.72 mol % CO, 0.06–0.16 mol % CO₂) than in those of the baseline tests (0.00–0.23 mol % CO, 0.04–0.05 mol % CO₂), indicating that stronger inhibition of HDS and HDN by competitive adsorption of CO and CO₂ is possible during co-processing. Also noted from Table 3 is that the gas products of the co-processing tests are higher in CH₄ concentration (0.38–1.06 mol % CH₄) than the baseline gas products (0.29–0.87 mol % CH₄), which point toward the presence of methanation reactions of CO and CO₂.^{37,38} CH₄ concentrations in general show a positive trend with respect to temperature, while CO and CO₂ appear to plateau over the reported range of temperature. This trend suggests that the net generation of CO and CO₂ is in balance with methanation reactions.

Deactivation of catalyst active sites caused by biocrude components and their reaction products is also likely to occur. The catalyst aging profile built from the check-back tests at 360 °C (shown in Figure 5) actually supports deactivation as the

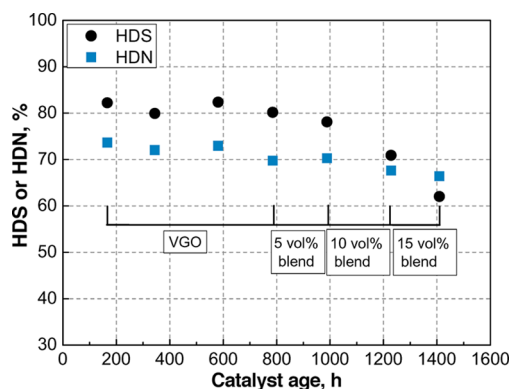


Figure 5. Catalyst aging profiles for HDS and HDN; check of catalyst performance using pure VGO at 360 °C. Feedstock labels below the data points denote the sequence of tests with different feedstocks over time.

main reason behind the observed trends seen in Figures 3 and 4. The check-back tests using the pure VGO feed are essential to compare the catalytic activity after each set of co-processing runs with the baseline values generated during the VGO runs, before introducing any biocrude blend into the reactor. As seen in Figure 5, HDS and HDN remain fairly stable during the runs with pure VGO up to 785 h on stream. After the tests with the 5 vol % blend, the check-back at 988 h reveals that HDS starts a slow decline. A more pronounced decay in HDS activity is observed after completion of the 10 and 15 vol % blend tests at about 1228 and 1409 h, respectively. The sharpest drop in HDS activity occurs after testing the 15 vol % blend, where about 8.9% of HDS activity is lost with respect to the previous check-back at 1228 h. Under normal conditions, as in the first 785 h of operation, the catalyst would not be expected to lose its activity at such a rate. This is a clear indication that the biocrude components added to the feed

deactivate the catalyst, particularly when the biocrude content in the feed exceeds 10 vol %. The loss in HDS activity with respect to the initial check-back test at 166 h is as high as 20.2%. Interestingly, HDN activity appears to be more stable than HDS during co-processing, with an overall loss of 7.2% with respect to the initial check-back test (166 h). Furthermore, the last check-back showing higher HDN than HDS (66.4% HDN vs 62.0% HDS) reveals an atypical trend for petroleum hydroprocessing. This apparent shift in catalyst selectivity caused by co-processing biocrude needs to be investigated further to assess operational impacts over the long run.

It is important to note that since the co-processing feed blends were tested sequentially, the results for the 10 and 15 vol % biocrude blends depicted in Figures 3 and 4 reflect the cumulative catalyst deactivation from the preceding co-processing runs. In other words, the HDS and HDN activity profiles of the 15 vol % blend also reflect the activity loss caused by the 5 and 10 vol % blends. Correction for catalyst deactivation can be applied for supplementary analysis of the activity loss in a scenario in which each biocrude blend is tested right after the baseline VGO runs, that is, at 780 h of catalyst age.

The above analysis highlights several practical impacts. To co-process HTL biocrude fractions obtained by distillation without any further chemical pretreatment, process severity will need to be increased accordingly to compensate for the effect of biocrude contaminants on catalyst activity. The degree to which operating conditions need to be adjusted will depend on the amount of biocrude in the hydroprocessor feed. The maximum amount of distilled biocrude that could be co-processed in such a manner would be in between 5 and 10 vol % at temperatures of 370 °C or above in this case. Beyond this range, accelerated catalyst deactivation and selectivity loss might become an issue in the long run, as demonstrated in Figure 5. On the other hand, the operational impacts outlined above are directly connected to the chemical properties of raw biocrude fractions, suggesting that a chemical upgrading step prior to co-processing is likely to improve co-processing efficiency. Partial hydrodeoxygenation is an option worth considering given its ability to convert not only oxygenated compounds in the distillable portion of biocrude but also heavy oligomers in residual fractions, which ultimately would improve miscibility in petroleum and maximize the biogenic liquid input yield for co-processing.

3.3. Impact of Co-processing on Hydrogen Consumption. Hydrogen consumption by hydroprocessing reactions was estimated based on a global hydrogen balance in the gas and liquid products, using the composition of gas products measured by online GC and the hydrogen contents in the feed and hydrotreated products. For visual purposes, calculated values of hydrogen consumption are presented in Figure 6 in relation to the primary reaction in the process, HDS in this case. Hydrogen consumption is found to vary between 385 and 856 scf/bbl as sulfur removal levels are

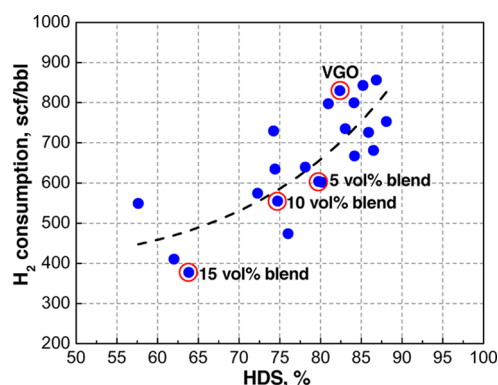


Figure 6. Hydrogen consumption as a function of HDS (all experiments). Data points for the tests with the different feed blends at 360 °C are labeled and marked with red circles.

increased from 60 to 90%. The set of hydrogen consumption data presented in Figure 6 carries a certain degree of scattering, which is mainly associated with measurement errors affecting hydrogen mass balance closure. Concerning the effect of biocrude co-processing on hydrogen consumption, the drop in HDS activity that comes with the addition of biocrude into the VGO feed leads to a proportional reduction in hydrogen consumption, as exemplified by the series of tests at 360 °C (data points in Figure 6 marked by red circles and with labels indicating feed blend). Therefore, if the HDS activity for co-processing the biocrude blends was to be maintained at the VGO baseline level by increasing process severity, hydrogen consumption is projected to be very similar to the baseline value in this case.

3.4. Quality of Co-hydroprocessed Products. The bulk properties of the hydroprocessed liquid products generated from the different feeds at 360 °C are presented in Table 4. As expected, products exhibit reduced contents of sulfur, nitrogen, and oxygen in relation to their respective feedstocks (see Table 1). Analysis of saturates, aromatics, and polars (SAP) shows

Table 4. Properties of Hydrotreated (HT) Products at 360 °C

property	HT-VGO	HT-5 vol % blend	HT-10 vol % blend	HT-15 vol % blend
density at 15.6 °C, g/cm ³	0.9295	0.9278	0.9286	0.9317
carbon, wt %	87.0	87.1	86.9	86.8
hydrogen, wt %	12.6	12.1	12.5	12.2
sulfur, wt %	0.6	0.6	0.8	1.1
trace nitrogen, wppm	817	883	921	954
oxygen, wt %	<0.1 ^a	<0.1 ^a	0.1	0.2
biogenic carbon, %		5	9	14
SAP Analysis				
saturates, wt %	50.0	49.3	51.5	47.2
aromatics, wt %	44.8	45.4	43.8	45.9
polars, wt %	5.2	5.3	4.7	6.9
Fractional Composition				
naphtha (IBP–204 °C), wt %	1.7	2.6	3.3	4.0
light gas oil (204–343 °C), wt %	10.5	12.5	13.8	15.3
vacuum gas oil (343 °C+), wt %	87.8	84.9	82.9	80.7

^aValues below the 0.1 wt % detection limit of the oxygen analyzer.

net generation of saturated hydrocarbons at the expense of reduced aromatics and polars. The products from the co-processing runs are of slightly lower grade than the VGO baseline in terms of heteroatom content, primarily owing to the effect of biocrude on catalyst activity. This deterioration in quality is consistent with the co-processing ratio.

In terms of fractional composition, it is noted that the co-processed products contain more distillate fractions (<343 °C) than the hydrotreated VGO, primarily because the biocrude distillate contained about 48 wt % of these fractions. The increase in these fractions in the co-processing product is more or less proportional to the amount of biocrude added into the feed. Figure 7 displays the full boiling point distribution profiles of the different products generated at 360 °C.

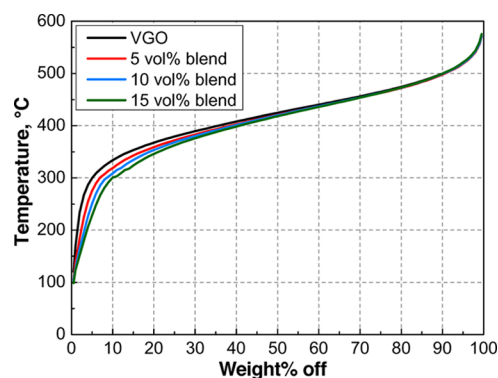


Figure 7. Boiling point distribution of liquid products generated at 360 °C.

Also shown in Table 4 are the biogenic carbon measurements in the co-processed liquid products. Results are expressed as the percentage of biogenic carbon relative to the total amount of carbon in the sample in accordance with ASTM D6866. The numbers are strikingly similar to the corresponding ratios of biocrude in the feed, indicating that the majority of the biogenic carbon in the feed was preserved in the liquid product. To elaborate on this point, biogenic carbon balance calculations were conducted for the co-processing runs at 360 °C, and the results are reported in Table 5. The first row

Table 5. Biogenic Carbon Balance for Co-processing Runs at 360 °C

calculated property	5 vol % blend	10 vol % blend	15 vol % blend
biogenic carbon in feed, g/100 g feed	4.04	8.07	12.10
biogenic carbon in product, g/100 g product	4.35	7.82	12.15
biogenic carbon in product, g/100 g feed	4.24	7.64	11.82
retention in product, %	105.0	94.7	97.7

shows the mass of biogenic carbon per 100 g of co-processing feed going into the reactor, estimated based on the total carbon content in the biocrude distillate (Table 1) and the mass ratio of biocrude distillate in the feed. The next row has the calculation of the amount of biogenic carbon per 100 g of liquid product output by using the biogenic carbon measurements and total carbon contents in co-processed products (Table 4). Because the entirety of liquid feed going through a hydroprocessor cannot be recovered as a liquid product due to

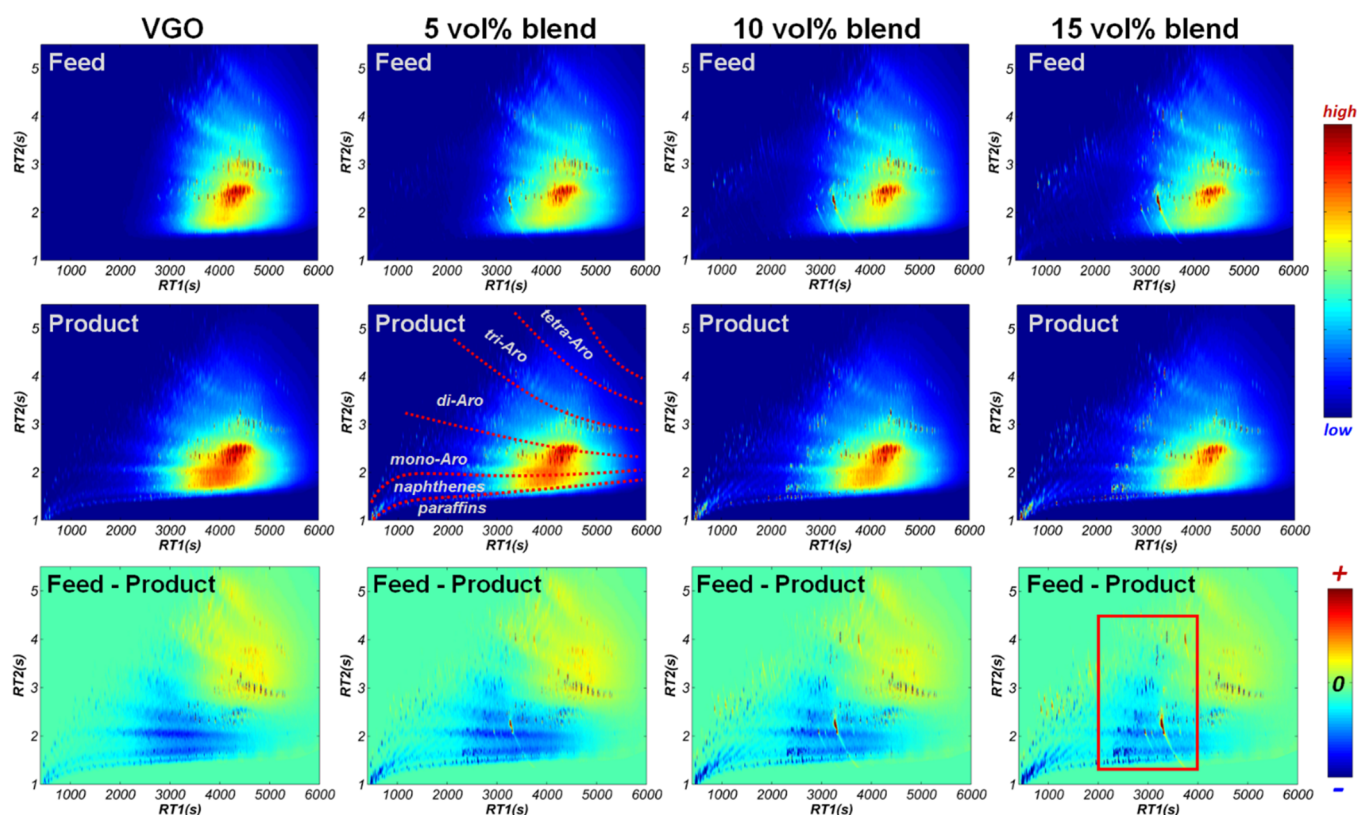


Figure 8. GC \times GC-FID chromatograms of the feedstocks (first row) and their respective liquid products generated at 360 °C (second row). The labels inside the chromatogram of the 5 vol % blend product indicate the regions of hydrocarbon types. The colors over the blue background refer to peak intensity, with red representing the most intense peaks. The third row displays GC \times GC-FID differential chromatograms highlighting the changes in hydrocarbon-type distribution from the feed to the product. The color scale on the right-hand side represents change in concentration relative to the feed: brown means decreased the most and deep blue means increased the most. The area marked by the red rectangle inside the differential chromatogram of the 15 vol % blend is analyzed further in Figure 9. RT1 refers to primary dimension and RT2 refers to secondary dimension.

Table 6. Hydrocarbon Class Composition of Hydrotreated (HT) Products at 360 °C

hydrocarbon class	HT-VGO	HT-5 vol % blend	HT-10 vol % blend	HT-15 vol % blend
<i>n</i> -paraffins, wt %	0.2	0.6	0.9	1.3
<i>iso</i> -paraffins, wt %	0.7	0.7	0.7	0.7
cycloparaffins, wt %	45.0	44.2	45.3	41.2
steranes, wt %	3.5	3.2	3.9	3.5
hopanes, wt %	0.7	0.7	0.6	0.6
monoaromatics, wt %	15.1	13.4	9.6	10.5
diaromatics, wt %	27.7	29.3	28.4	30.4
triaromatics, wt %	6.9	7.9	10.3	11.7
tetraaromatics, wt %	0.2	0.2	0.2	0.3

gas make, biogenic carbon calculations for the products must be referred to the feed for consistency in the analysis. This is done in the third row by multiplying these values by the measured liquid recoveries (97.3–97.7 wt %). The last row presents the biogenic carbon retention in product, here defined as the percentage of biogenic carbon transferred from the feed to the liquid product. It follows that the maximum theoretically possible biogenic carbon retention is 100%, but the calculated values can go over this limit due to influence of experimental errors. With retentions estimated at 94.7–105.0%, one could conclude that nearly all of the biogenic carbon added to the feed is retained in the liquid product, with minimal loss to gas. However, the ASTM D6866 testing standard assigns a $\pm 3\%$ absolute error to all measurements, which gives our calculations a significant margin of uncertainty. For example,

the 5 vol % blend product would be considered to have from 2 to 8% biogenic carbon with a mean of 5%, so this would translate into biogenic carbon retentions between 42.0 and 167.9%, the upper value being well beyond the theoretical limit.

3.5. Detailed Product Characterization. GC \times GC characterization was conducted to gain better understanding of the composition of co-processed products. Figure 8 presents three sets of GC \times GC-FID chromatograms. The top and the middle panels depict contour maps for the four feedstocks and their corresponding hydrotreated products at 360 °C, respectively. In both cases, the GC \times GC instrument was configured with normal polarity column combination, indicating that the separation of compounds took place on a nonpolar (VF-5ht) \times semipolar (BPX-50) column set. The

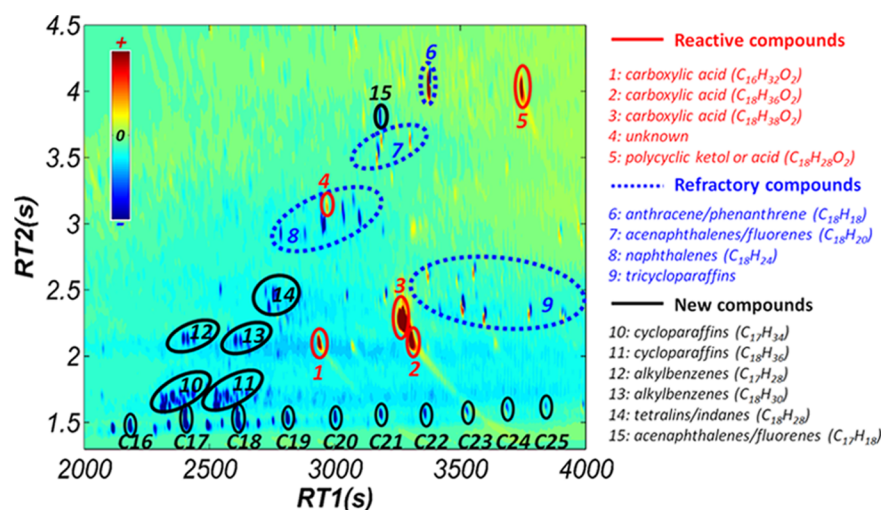


Figure 9. Supplementary GC \times GC-FID differential chromatogram of the 15 vol % blend, as marked in Figure 8. The color scale inside the figure represents a change in concentration relative to the respective feed: brown means decreased the most and deep blue means increased the most. Region numbers correspond to the proposed compounds identified in the legend list on the right-hand side. RT = retention time.

differences in chemical composition of the 5, 10, and 15 vol % blends (see the top panel in Figure 8) are related to the addition of biocrude components into VGO. The clearest example of this is the appearance of a prominent peak at RT1 \sim 3200 s and RT2 \sim 2.4 in all blends. We presume this peak to be a C_{18} fatty acid. The presence of long-chain fatty acids in HTL biocrude has in fact been reported.³⁵ The concentrations of the various hydrocarbon classes in the hydrotreated products displayed in the middle panel of Figure 8 are given in Table 6. For reference, the regions of each hydrocarbon class are delineated and labeled on the chromatogram of the 5 vol % blend product. From Table 6, it is seen that the co-processed products are in essence more paraffinic and higher in di- and triaromatics than the hydrotreated VGO. The additional paraffins in the co-processed products likely originate from the fatty acids in biocrude, whereas the extra aromatics could derive from the abundant aromatic oxygen compounds in biocrude.

The bottom row in Figure 8 presents chromatographic contour maps obtained by subtracting the chromatograms of the hydrotreated products (middle panel) from the chromatograms of their respective feedstocks (top panel). This was done to enhance visualization of the compositional changes during co-processing. The red/brown peaks indicate the species that were consumed the most by hydrotreating, while the blue peaks depict the appearance of reaction products. With this format, it is clearly seen that hydrotreating shifts hydrocarbon-type composition from being highly aromatic to more saturated, with paraffins standing out for the co-processed products. The region marked by the red rectangle on the differential chromatogram of the 15 vol % blend (bottom panel, Figure 8) is analyzed in more detail in Figure 9.

Examination of the area shown in Figure 9 using mass spectrometry information allowed us to recognize three distinct groups of compounds revealing potential chemical pathways during co-processing. On the right-hand side of the chromatogram, we present a list of several proposed compounds, here categorized as reactive, refractory, and new compounds. Reactive compounds refer to those that are present in the feedstock and that quickly disappeared during hydroprocessing. Carboxylic acids from biocrude are the main

components of this group and are considered the source of the additional paraffins in co-processed products, as shown in Table 6. The refractory group is comprised of diaromatic (e.g., C_{18} naphthalene and fluorene), triaromatic (C_{18} phenanthrene), and tricycloparaffinic species existing in the feedstock, which concentrations do not change much or may actually increase after hydroprocessing. The small variations in concentration indicate that these species are mostly at equilibrium. The increased presence of certain aromatics suggests that there is contribution from oxygenated aromatic species in biocrude. This is consistent with the trend in Table 6, showing that the co-processed products are richer than the hydrotreated VGO in di- and triaromatics. Newly formed species include C_{17} – C_{18} cycloparaffins, monoaromatics (tetralins and alkylbenzenes), and fluorenes. Given that co-processing decreases selectivity toward monoaromatics and cycloparaffins, as per Table 6, the contribution of biocrude to these newly formed products appears to be low. In summary, this brief analysis illustrates that the incorporation of biocrude into the hydroprocessor feed modifies regular reaction schemes, resulting in products differing in hydrocarbon-type composition.

4. CONCLUSIONS

In this study, we assessed the feasibility of co-hydroprocessing HTL biocrude with VGO on a continuous pilot scale. Our results support the following conclusions:

- Co-processing HTL biocrude distillate without any prior chemical upgrading is possible within a specific blending range. Our observations indicate that the ratio of biocrude that can be co-hydroprocessed with VGO is below 10 vol % at temperatures of 370 °C or above.
- Adding 10 vol % biocrude or more into the hydroprocessor feedstock decreases HDS and HDN activities. This is mainly attributed to catalyst deactivation by contaminants present in the biocrude and possibly the inhibitory effect of the CO and CO_2 produced from decarbonylation and decarboxylation reactions.
- Depending on the amount of biocrude added into the feed, process severity will need to be adjusted to maintain HDS and HDN activities at the baseline level.

- The tested biocrude blends are likely to have a similar hydrogen consumption to give the same HDS, as the VGO baseline.
- The presence of biogenic carbon in co-processed liquid products was confirmed by radiocarbon analysis. Biogenic carbon balance calculations appear to indicate that nearly all of the biogenic carbon is transferred to the liquid product, yet the uncertainty of these estimations is elevated.
- GC × GC analysis revealed that co-processing yields the product with higher paraffin and di- and triaromatic contents.
- It is recommended that biocrude chemical pretreatment approaches, such as partial hydrodeoxygenation, be explored as a means of improving co-processing performance.

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Notes

The authors declare no competing financial interest.

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