

Production of Renewable Liquid Fuels by Coprocessing HTL Biocrude Using Hydrotreating and Fluid Catalytic Cracking

Yi Zhang and Anton Alvarez-Majmudov*

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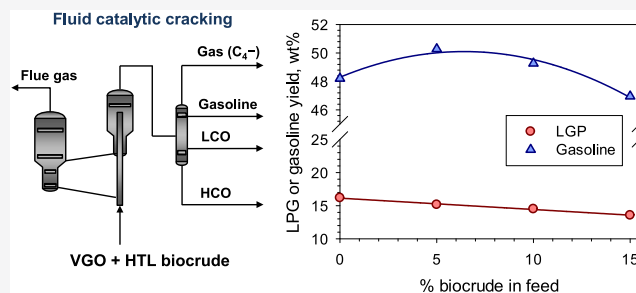
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ABSTRACT: In this study, we explore coprocessing of hydrothermal liquefaction (HTL) biocrude with vacuum gas oil (VGO) in the fluid catalytic cracking (FCC) process. Coprocessing experiments were conducted using an advanced cracking evaluation FCC laboratory unit. Four sets of experiments were conducted: one with pure VGO to set the baseline performance and three sets with different VGO/HTL biocrude blends (5, 10, and 15% biocrude). Each set of tests covered a range of catalyst-to-oil ratios with temperature fixed at 510 °C. Prior to the FCC tests, the VGO and biocrude blends were hydrotreated in a continuous pilot plant to reduce the levels of heteroatoms, in an attempt to represent a refinery scheme with an FCC pretreat hydroprocessing unit. During the FCC tests, the biocrude blends showed lower conversion levels with respect to the baseline as a result of having more nitrogen and oxygen compounds that could have acted as catalyst inhibitors. Nevertheless, at a given conversion, the selectivity toward gasoline improved when the coprocessing ratio was 5%. The coprocessed gasoline products were nearly identical in terms of hydrocarbon type composition to the one from VGO at high conversion. The 10 and 15% biocrude blends showed a pronounced tendency to yield more light cycle oil, dry gas, and coke than VGO. As a whole, the study suggests that the coprocessing ratio for HTL biocrude should optimally be around 5% to minimize impacts on product yield distribution.



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1. INTRODUCTION

Coprocessing refers to a prospective pathway for producing renewable liquid fuels whereby biogenic feedstocks are converted together with petroleum into finished fuel products in existing refinery units.^{1,2} Aside from eliminating the need to invest in biorefining infrastructure, coprocessing is strategic for oil refineries in that it can help them reduce their carbon intensity and comply with government regulations. A variety of biogenic feedstocks can be used for this purpose, among which are vegetable oils, waste cooking oil, animal fats, and more recently bio-oils/biocrudes derived from the thermochemical conversion of a range of biomass resources, such as forest residues, agriculture wastes, sewage sludge, and algae. Coprocessing of lipid feedstocks (cooking oils, grease, fats) can be done with relative ease³ and has already been accomplished at commercial scale,^{4,5} whereas coprocessing of biocrudes has been found to be much more complicated given their complex chemical composition.^{6,7} Nevertheless, there is a need to find ways to incorporate biocrudes into the coprocessing feed pool as they become available in commercial quantities to address the long-term sustainability concerns of lipid feedstocks.

Among the potential cut-in points for biogenic feedstocks within a refinery, the fluid catalytic cracking (FCC) process stands out in current technical literature documenting the

advances in applying coprocessing in refineries.^{1,2,8,9} Coprocessing through an FCC unit primarily seeks to add renewable content to the gasoline pool in a refinery, although other FCC products like light cycle oil and petrochemical feedstock components will also collect part of this renewable material. The strengths of the FCC process in the context of coprocessing are that it does not require hydrogen and the catalyst is continuously regenerated, which is particularly important for managing any negative effects of biogenic oxygen species on the catalyst. Lipid feedstocks, being constituted of triglycerides and free fatty acids, are suitable for direct FCC coprocessing given their good miscibility with vacuum gas oil (VGO) and overall cracking reactivity.⁸ Coprocessing of lipid feedstocks tends to increase conversion levels in FCC but typically yielding less fuel products.^{9–11} Pyrolysis bio-oils, the most studied form of bio-oil, are much more difficult to deal with because of their elevated oxygen content (up to 40 wt

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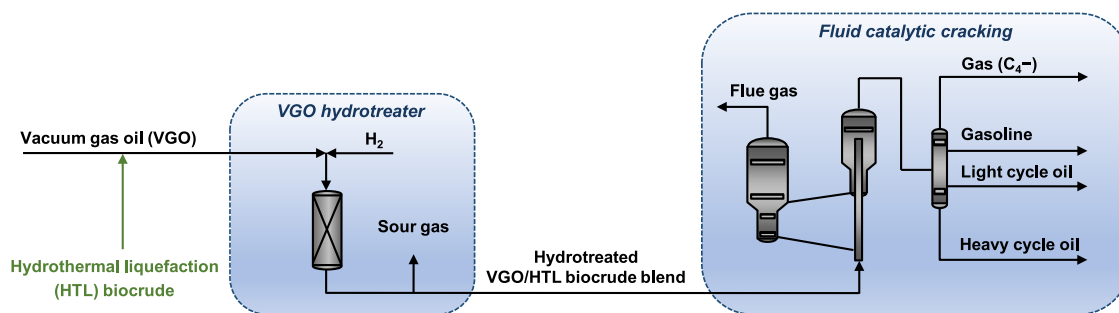


Figure 1. Proposed FCC coprocessing scheme.

%),¹² which imparts their poor miscibility with petroleum distillates and chemical instability during processing.⁷ Severe plugging issues and higher yields of undesirable products, such as coke and dry gas, have been typically observed in FCC coprocessing tests with pyrolysis bio-oils.^{9,13–16} Some studies^{17–21} concur on the idea that pyrolysis bio-oils require prior hydrodeoxygenation (HDO) to enable more efficient coprocessing.

Coprocessing of biocrudes produced by hydrothermal liquefaction (HTL) has not been studied as extensively as lipid feedstocks and pyrolysis bio-oils.^{22–29} While HTL biocrudes have lower oxygen content (generally below 15 wt % oxygen)^{30,31} and are more chemically stable than pyrolysis bio-oils, they pose similar challenges in terms of processability. They have been observed to affect catalytic performance to some extent when coprocessed with VGO through FCC,²⁵ hydrotreating,²⁷ and hydrocracking.²⁸ In most of these studies,^{25–28} the raw HTL biocrude was distilled to remove high boiling components having a tendency to form coke under typical FCC or hydroprocessing conditions and causing miscibility problems with petroleum distillates. The study by Mathieu et al.²⁵ showed that FCC coprocessing of HTL biocrude distillate with VGO in ratios higher than 10% yields more coke and dry gas. The study also demonstrates that subjecting the HTL biocrude to HDO pretreatment remedies this issue, thus enabling higher FCC coprocessing ratios. Other relevant studies^{22–24} have also recommended treating HTL biocrude via HDO to improve its miscibility with petroleum and reduce equipment corrosion.

In previous research,^{27,28} we examined a potential coprocessing scheme where HTL biocrude from woody biomass was first co-hydrotreated in admixture with VGO to reduce sulfur, nitrogen, and oxygen levels before going into a hydrocracking unit or, alternatively, an FCC unit. Pilot plant tests suggested that within certain boundaries it is feasible to coprocess HTL biocrude with VGO through hydrotreating, followed by hydrocracking. In continuation of this research, this study explores coprocessing of HTL biocrude in the FCC process after previously undergoing cohydrotreating with VGO, as illustrated in Figure 1.

2. EXPERIMENTAL SECTION

2.1. Materials. The test blends used in the FCC coprocessing experiments were constituted of VGO (~343 to 524 °C) from Canadian oil sands bitumen and HTL biocrude from forest residue biomass provided by Steeper Energy. The test blends and HTL biocrude underwent a series of treatment steps. The as-is HTL biocrude was first pretreated by filtration to remove any particulate matter, as well as by distillation under vacuum to drive off any associated water and separate heavy biocrude components exceeding

the end boiling point of VGO (524 °C). This form of pretreatment was shown effective in improving the biocrude's processability and miscibility with petroleum.²⁷ The treated HTL biocrude distillate was blended with the straight-run VGO in volume ratios of 5, 10, and 15 vol % biocrude. The three resulting biocrude blends and the straight-run VGO were hydrotreated to bring down their sulfur and nitrogen concentrations, as done in refinery schemes having an FCC pretreat hydroprocessing unit. Hydrotreating was conducted in a continuous pilot plant unit having a tubular reactor (length 105 cm and diameter 0.9 cm), which was set up to operate in upflow mode. A commercial NiMo/Al₂O₃ catalyst for VGO hydrotreating was used. The operating conditions for the hydrotreating step were the following: liquid hourly space velocity (LHSV) 1.5 h⁻¹, temperature 360 °C, pressure 6.9 MPa, and hydrogen-to-oil ratio 800 NL/L. The details of the HTL biocrude pretreatment and cohydrotreating experiments can be found elsewhere.²⁷

A commercial equilibrium catalyst (ECAT) from a refinery was employed for the FCC coprocessing tests. The catalyst was screened using 60 and 400 Tyler mesh sieves, as per the recommendation from the catalytic cracking test unit manufacturer. The sieved catalyst particles were calcined at 600 °C for 4 h to remove any carbonaceous residue and moisture.

2.2. Coprocessing Experiments. The FCC coprocessing experiments were conducted using an advanced cracking evaluation (ACE) laboratory test unit from Kayser Technologies.³² The unit is configured to simulate FCC and spent catalyst regeneration after the reaction is completed, all in the same test reactor using a cyclic mode of operation. The unit is equipped with six catalyst hoppers and six liquid product receivers, allowing conducting six tests in a row. The reactor itself is a stainless steel tube having an internal diameter of 1.6 cm and a tapered conical bottom, as shown in Figure 2. Fluidization of the catalyst is achieved by flowing nitrogen from the bottom of the reactor. The feed sample is injected from the top, through a line extending downwards near the bottom of the reactor. The cracked product vapor exiting the reactor is condensed and collected in a liquid product receiver. The noncondensable products go to an online gas chromatography (GC) instrument for gas composition analysis. Once a test is completed, the spent catalyst is stripped with nitrogen and the deposited coke is burned with air at temperatures of 700 °C or above. The CO₂ that is released is quantified using an infrared gas analyzer to estimate coke yield.

Four sets of experiments were conducted, one with each of the three hydrotreated biocrude blends (5, 10, and 15% biocrude) and one with the hydrotreated VGO (HT-VGO) to set the baseline performance of the system. Each set consisted of six tests covering a range of catalyst-to-oil (CTO) ratios (4, 5, 6 (twice), 8 and 10 g/g) to generate data at different conversion levels. The prescribed CTO ratio was achieved by adjusting the feed sample injection time, with the amount of ECAT per test batch constant at 9 g and the feed injection rate fixed at 1.2 g/min. All FCC experiments were done at a constant temperature of 510 °C and atmospheric pressure. For the catalyst regeneration part of each test, stripping time was set to be 7 times the feed sample injection time while the regeneration temperature was fixed at 715 °C. On average, mass recovery throughout the tests was 97.7% with a standard deviation of 1.5%.

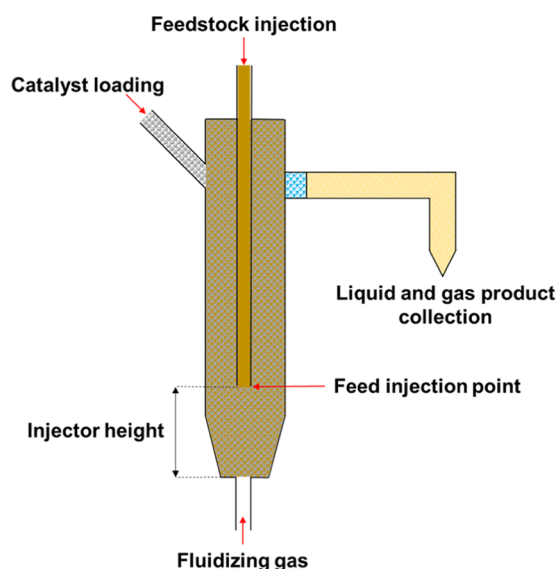


Figure 2. Schematic of an ACE unit fluidized bed reactor.

The four feedstocks and their cracked liquid products were characterized using standard analytical methods. Feedstock analysis included the following: liquid density (ASTM D4052), boiling point distribution by simulated distillation (SimDis) (ASTM D2887), elemental analysis C, H, N (ASTM D5291C), oxygen content by direct determination using an Elementar oxygen analyzer (in-house method), sulfur by X-ray fluorescence (ASTM D4294), microcarbon residue (MCR) (ASTM 4530), and hydrocarbon class composition by two-dimensional gas chromatography with flame ionization detection (GC × GC-FID). The details of the GC × GC-FID analysis are provided elsewhere.²⁷ All liquid products were analyzed for boiling point distribution using simulated distillation to obtain FCC liquid product yields. Hydrocarbon type composition analysis of FCC gasoline fractions was done using gas chromatography–vacuum ultraviolet spectroscopy (GC–VUV) (ASTM D8071). The GC–VUV instrument (VUV Analytics, Inc.) was comprised of an Agilent 7890 gas chromatograph with an Agilent 7683 autosampler and a VGA-101 VUV detector. Biogenic carbon content measurements using radiocarbon analysis (ASTM D6866) were performed for the liquid products deriving from the biocrude blends.

3. RESULTS AND DISCUSSION

3.1. Feedstock Properties. The properties of HT-VGO and the three hydrotreated biocrude blends are provided in Table 1. Boiling point distribution curves are shown in Figure 3. For reference, selected properties of the untreated VGO and

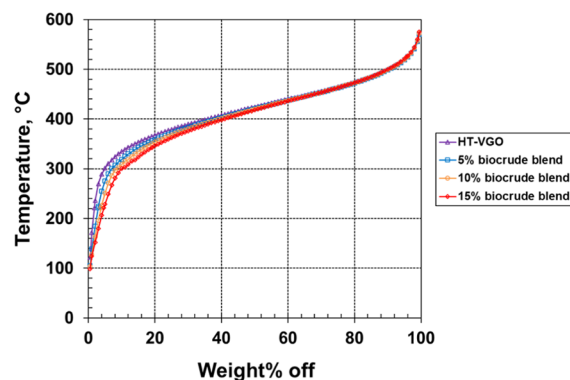


Figure 3. Boiling point distribution curves of HT-VGO and the hydrotreated biocrude blends.

HTL biocrude are also included in Table 1. In comparing the VGO before and after hydrotreating, it is seen that heteroatom (sulfur, nitrogen, and oxygen) levels have been significantly reduced. Hydrotreating also visibly changes hydrocarbon composition, increasing the proportion of saturates at the expense of aromatics and polars. All of these changes in quality are considered beneficial for FCC.³³ The hydrotreated biocrude blends differ from HT-VGO in that they show higher levels of heteroatoms, which trend upwards in relation to the biocrude ratio in the blend. This is because during the hydrotreating stage catalytic activity was observed to be inhibited proportionally to the amount of HTL biocrude in the feed blend.²⁷ Thus, the blend having 15% biocrude is the highest in heteroatoms (11000 wppm sulfur, 954 wppm nitrogen, and 2100 wppm oxygen), whereas HT-VGO is the lowest (7200 wppm sulfur, 866 wppm nitrogen, and <1000 wppm oxygen). In terms of hydrocarbon class composition, the biocrude blends are slightly more paraffinic (1.3–1.9 wt %) and higher in di- (28.4–30.4 wt %) and polyaromatics (8.1–12.0 wt %) than HT-VGO (0.8 wt % paraffins, 27.7 wt % diaromatics, and 7.2 wt % polyaromatics). The extra paraffins

Table 1. Properties of VGO, HTL Biocrude, HT-VGO, and Hydrotreated Biocrude Blends^b

property	VGO	HTL biocrude	HT-VGO	5% blend	10% blend	15% blend
density at 15.6 °C (g/cm ³)	0.9759	1.0536	0.9296	0.9278	0.9286	0.9317
carbon (wt %)	84.8	80.0	86.7	87.1	86.9	86.8
hydrogen (wt %)	11.1	9.4	11.9	12.1	12.5	12.2
sulfur (wppm)	36 000	96	7200	6840	8120	11 000
nitrogen (wppm)	3000	800	866	883	921	954
oxygen (wppm) ^a	5000	10 520	<1000	<1000	1000	2100
MCR (wt %)		49.7	0.04	0.04	0.07	0.04
Hydrocarbon class composition						
paraffins (wt %)			0.8	1.3	1.6	1.9
cycloparaffins (wt %)			49.2	48.0	49.9	45.3
monoaromatics (wt %)			15.1	13.4	9.6	10.5
diaromatics (wt %)			27.7	29.3	28.4	30.4
polyaromatics (wt %)			7.2	8.1	10.5	12.0

^aThe detection limit of the oxygen analyzer is 1000 wppm. ^bVGO, vacuum gas oil; HTL, hydrothermal liquefaction; HT-VGO, hydrotreated vacuum gas oil; MCR, microcarbon residue.

and aromatics in the biocrude blends were previously attributed to C_{18} fatty acids and aromatic oxygen species present in the original HTL biocrude, respectively.²⁷ With respect to boiling point distribution (Figure 3), the hydro-treated biocrude blends show more light material boiling below 343 °C than HT-VGO, mostly because the original HTL biocrude distillate added to the starting feed blends had ~48 wt % of such low boiling material.

3.2. Impacts on FCC Performance. Figure 4 shows how overall conversion at different CTO ratios is impacted by the

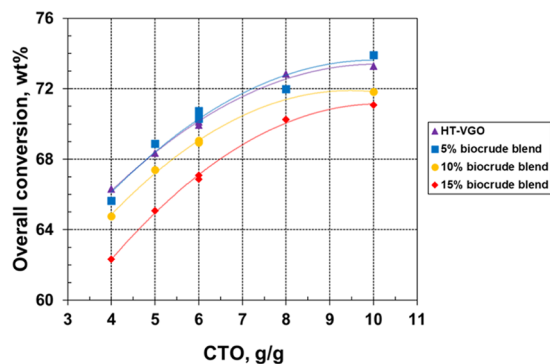


Figure 4. Overall conversion of HT-VGO and the biocrude blends as a function of the CTO ratio at 510 °C reaction temperature.

addition of biocrude. Conversion here is defined as the percentage of the feed boiling above 221 °C that is converted into gasoline (35–221 °C), liquefied petroleum gas (LPG) (C_3 – C_4), dry gas (C_1 – C_2 , H_2 , and H_2S), and coke. It is a key parameter reflecting the ability of the FCC process to react a given feedstock at certain conditions.

As seen in Figure 4, increasing the CTO ratio leads to higher conversion levels by increasing the concentration of active sites in the FCC reactor. At the highest CTO ratio (10 g/g), conversion starts leveling off, which is an indication that the crackable components in the feed have been nearly exhausted. This means that there would be no benefit in increasing the CTO ratio beyond this point. In comparing different feedstocks, HT-VGO and the 5% biocrude blend perform quite similarly in terms of conversion, whereas the 10 and 15% biocrude blends give proportionally lower conversion levels. One data point of the 10% biocrude blend data set (CTO ratio 8 g/g, 72.5% conversion) was identified as an outlier and excluded from further analysis. Based on the characteristics of each feedstock presented in Table 1, similarities between HT-VGO and the 5% biocrude blend would explain why these two give comparable conversion in the FCC process. The drop in conversion when the biocrude ratio in the feed is 10% or higher is attributed to the increasing levels of nitrogen and oxygen. Nitrogen is a well-known FCC catalyst poison,^{34,35} while oxygen species in bio-oils have been found to form coke causing the deactivation of FCC catalysts.^{36,37}

Figure 5 shows gasoline yield profiles for HT-VGO and biocrude blends as a function of conversion. All feedstocks appear to follow the typical pattern where gasoline yield peaks at a certain conversion level and then slowly declines as conversion goes up due to the overcracking of gasoline components into gas products and coke. For the whole set, the maximum gasoline yield (48–50 wt %) occurs approximately at or past the 70–72% conversion mark. The fact that the four feedstocks are visibly offset from each other is an indication of

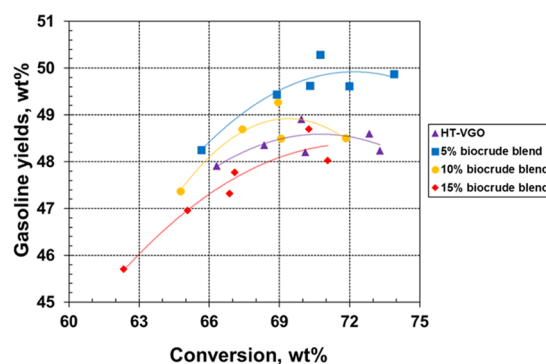


Figure 5. Gasoline yields vs conversion.

a shift in the feedstock reactivity profile as a result of introducing biocrude. The 5% biocrude blend appears to be slightly more selective toward gasoline than HT-VGO, whereas the 10% blend gives more gasoline than HT-VGO only at conversions below 70%. This can be explained by the fact that the biocrude blends initially contained more light, potentially more crackable material, as indicated by their boiling point distribution profiles (Figure 3). Below 70% conversion, the 15% biocrude blend yields less gasoline, but at higher conversions, it seems to be in the similar range (48–49 wt % gasoline) as HT-VGO and the 10% blend. Therefore, the 10 and 15% biocrude blends have a minimum impact on gasoline selectivity in the high conversion range (70–73%).

Based on the hydrocarbon class composition reported in Table 1, it is interesting to note that HT-VGO is modestly higher in gasoline precursors (defined as the cumulative amount of paraffins, cycloparaffins, and monoaromatics) than any of the biocrude blends (65.1 wt % for HT-VGO vs. 57.7–62.2 wt % for biocrude blends). Nevertheless, the trends in Figure 5 appear to indicate that the gasoline precursors in the biocrude blends are more reactive to some extent. This could be related to the fact that the biocrude blends have more low boiling material (<343 °C), and so consequently, their gasoline precursors are overall lighter than the ones in HT-VGO.

Along with gasoline, LPG is another valuable FCC product that is used in alkylation and as a petrochemical feedstock. Figure 6 shows that the biocrude blends consistently yield less LPG than HT-VGO, implying that the addition of biocrude to the feed reduces LPG selectivity in relation to HT-VGO. Interestingly, the LPG data sets for the three biocrude blends are overlapped, which suggests that LPG selectivity is independent from the coprocessing ratio. The loss in LPG selectivity implies that the reactions leading to the formation of

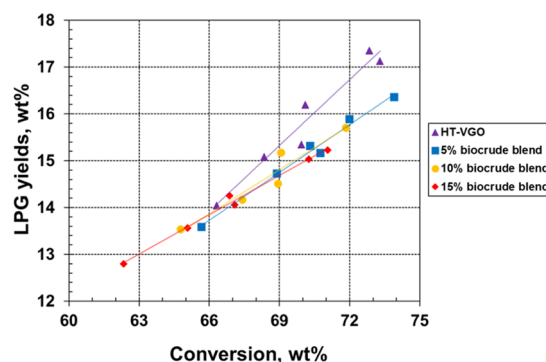


Figure 6. LPG yields vs conversion.

LPG products, mainly dealkylation reactions and cracking of paraffins, become less prevalent in the biocrude blends. The contribution of paraffins to the observed LPG trends is expected to be minimum in this case, considering that HT-VGO and the three biocrude blends are very low in paraffinic content, as shown in Table 1. A possible explanation is related to the fact that the biocrude blends have an increased ratio of aromatics deriving from HTL biocrude, specifically diaromatics and polyaromatics (see Table 1). Comprehensive characterization of aromatic hydrocarbons and oxygenated aromatic species in HTL biocrude³⁸ have shown the prevalence of structures with multiple methyl and/or ethyl branches, which makes it reasonable to presume that aromatics from HTL biocrude are less likely to release C₃–C₄ fragments through dealkylation reactions. Therefore, the shift in LPG selectivity during coprocessing can be attributed to the structural nature of HTL biocrude.

Light cycle oil (LCO) is a middle distillate product with a boiling range 221–343 °C, rich in aromatics, and with relatively high sulfur content. Because of these characteristics, it requires hydrotreating before it can be used as a diesel blendstock. As shown in Figure 7, LCO yield is minimized by

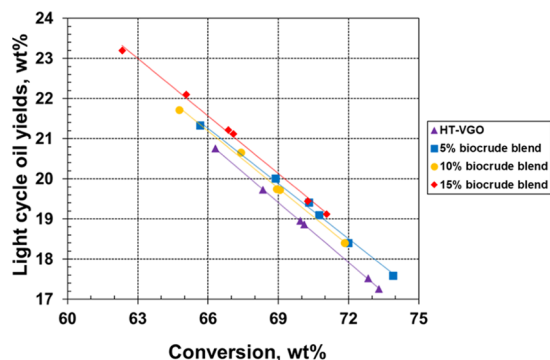


Figure 7. LCO yields vs conversion.

increasing conversion in the FCC unit. LCO in essence is an intermediate FCC product, which means that under the conditions used in this study the rate of consumption of LCO components far exceeded the rate of LCO generation from high boiling material. In terms of the impact of coprocessing, the biocrude blends give up to 1 wt % more LCO than HT-VGO at a given conversion, almost in proportion to the amount of biocrude in the feed blend. This is consistent with the fact that the biocrude blends are richer in diaromatics (Table 1), which are considered as LCO precursors in FCC.

Adjacent to LCO, heavy cycle oil (HCO) constitutes the unconverted >343 °C fraction of the liquid product. Higher conversions in the FCC unit lead to a reduction in HCO yield, as illustrated in Figure 8. At any given conversion, the biocrude blends show 1.0–1.5 wt % less HCO than HT-VGO, with the lowest HCO selectivity being observed for the 15% biocrude blend. This is evidence that the >343 °C fraction of the biocrude blends is more reactive than that of their HT-VGO counterpart. To some extent, this aligns with the observed trends showing that the biocrude blends give more LCO (Figure 7) and, in some cases, more gasoline (Figure 5) at a given conversion.

The increased reactivity of the >343 °C fraction of the biocrude blends observed in Figure 8 also has an effect on coke yields. From Figure 9, it can be observed that the 10 and 15%

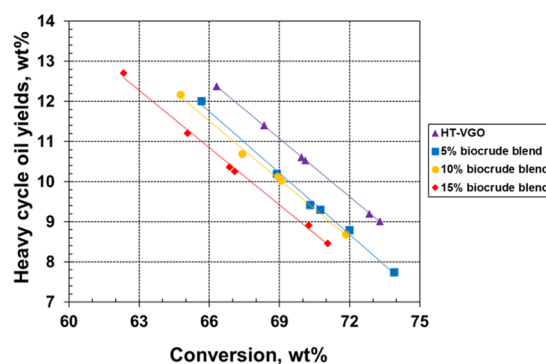


Figure 8. HCO yields vs conversion.

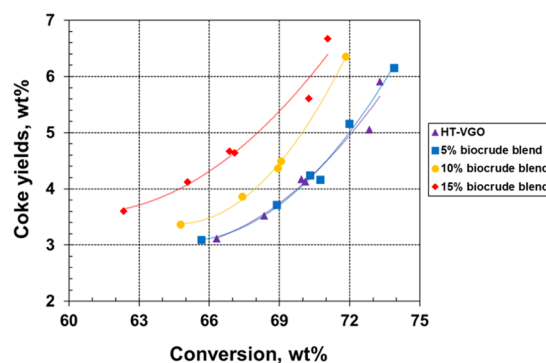


Figure 9. Coke yields vs conversion.

biocrude blends yield up to ~1.5 wt % more coke than HT-VGO and the 5% blend at a given conversion. The said increment in coke yield most likely originates from the additional polyaromatics in the biocrude blends, particularly in the 10 and 15% blends (see Table 1). Because the majority of these polyaromatics species reside in the high boiling >343 °C fraction, their conversion into coke adds to the observed reduction in HCO. Moreover, it is also plausible that a significant portion of the excess oxygen in the biocrude blends is found within these polyaromatic species as furan and phenol functionalities, contributing further to coke formation.³⁸ Since coke itself is a catalyst deactivation agent, the increased coking tendency of the biocrude blends explains why in Figure 4, at a given CTO ratio, the biocrude blends give lower conversion relative to HT-VGO.

Commercial FCC units are operated at a constant coke level to provide enough heat for the process. Figure 10 shows the

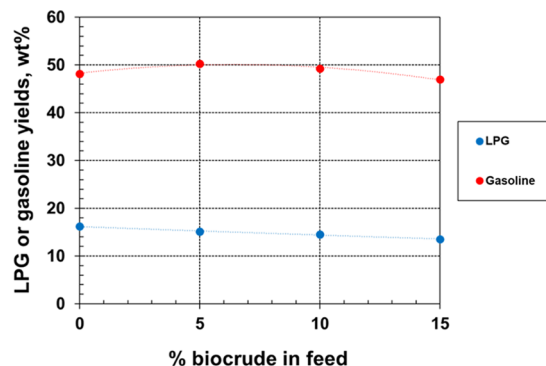


Figure 10. LPG and gasoline yield vs % biocrude in the feed at ~4 wt % coke.

LPG and gasoline yields as a function of the percentage of biocrude in the feed at a fixed coke level of approximately 4 wt %. Under such conditions, the effect of coprocessing appears rather small, and there seems to be an optimum at 5% biocrude.

Coprocessing HTL biocrude also has an effect on FCC dry gas yields (C_1 – C_2 , H_2 , and H_2S). As observed from Figure 11,

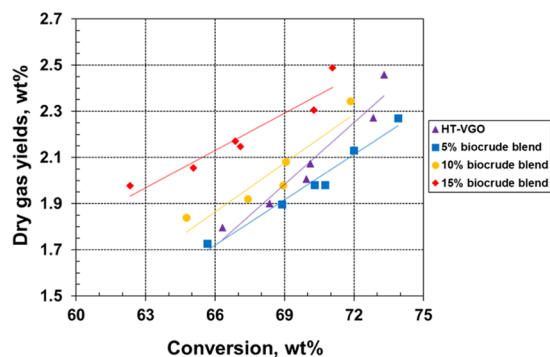


Figure 11. Dry gas yields vs conversion.

increasing conversion inevitably leads to more undesirable dry gas. Having 10% biocrude or more in the feed results in up to ~0.2 wt % more dry gas make. Since dry gas, in theory, can arise from both the cracking of high boiling components and overcracking of products like gasoline and LPG,³⁹ it is more difficult to identify the origin of the excess dry gas generated by the 10 and 15% biocrude blends. The dry gas yield breakdown for the four feedstocks at ~70% conversion provided in Table 2 reveals practically no changes in terms of H_2 , H_2S , methane,

Table 2. Dry Gas Yield Breakdown at ~70% Conversion

component	HT-VGO	5% blend	10% blend ^a	15% blend
hydrogen (wt %)	0.1	0.1	0.1	0.1
hydrogen sulfide (wt %)	0.2	0.1	0.2	0.2
methane (wt %)	0.6	0.6	0.6	0.6
carbon monoxide (wt %)	0.0	0.0	0.0	0.0
carbon dioxide (wt %)	0.1	0.1	0.2	0.2
ethane (wt %)	0.4	0.4	0.4	0.4
ethylene (wt %)	0.7	0.7	0.7	0.8
total dry gas (wt %)	2.1	2.0	2.2	2.3

^a10% blend data at ~70% conversion obtained by average interpolation.

and ethane; however, some differences are seen for CO_2 and ethylene. The 10 and 15% blends generate more CO_2 as a consequence of oxygenated components in the HTL biocrude. The extra ethylene shown by the 15% blend is likely attributable to the structural nature of HTL biocrude components, which are characterized by aromatics with relatively short alkyl substituents. Earlier we hypothesized that this was the reason behind the reduced selectivity for LPG, so it is possible that the structure of HTL biocrude aromatics could actually favor the generation of shorter fragments through dealkylation reactions. Gasoline overcracking could also be a contributor since all tested feedstocks reached a plateau in gasoline yield (Figure 5). However, this effect is harder to distinguish since the maximum gasoline yield in all cases was achieved in a very narrow conversion range (70–72%).

Taken together, these trends suggest that the HTL biocrude blending ratio for FCC coprocessing should optimally be set to 5% to minimize unfavorable changes in product yield structure. This is considering that the HTL biocrude had undergone cohydrotreating with VGO to reduce heteroatom levels prior to FCC. Coprocessing at higher ratios (10% or more) would likely require increasing severity in the FCC pretreat hydroprocessing unit to bring biocrude blend quality closer to that of the baseline FCC feed.

3.3. Gasoline Composition. The hydrocarbon type composition of the FCC gasoline fractions produced at two CTO ratios (10 and 4 g/g) are presented in Figures 12 and 13.

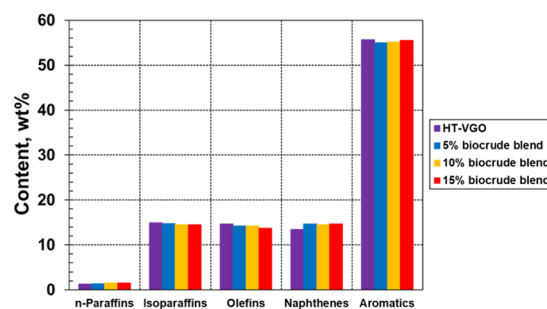


Figure 12. FCC gasoline hydrocarbon type composition at CTO ratio = 10 g/g.

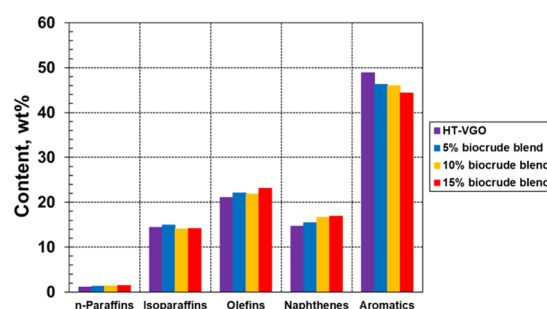


Figure 13. FCC gasoline hydrocarbon type composition at CTO ratio = 4 g/g.

The GC–VUV instrument had a prefractionator so that the gasoline fraction could be separated out of the total liquid product sample upon injection. Figure 12 shows that at a CTO ratio of 10 g/g there is virtually no difference between the coprocessed gasoline fractions generated from the biocrude blends and the one from HT-VGO. The four gasoline fractions are predominantly aromatic (55.0–55.6 wt %), with almost equal amounts of isoparaffins (14.5–15.0 wt %), olefins (13.7–14.7 wt %), and naphthenes (13.4–14.7 wt %). The concentration of *n*-paraffins is minor (1.3–1.5 wt %), mostly because the tested feedstocks were very low in *n*-paraffins (see Table 1). The great similarity in gasoline composition for this particular coprocessing scheme strongly suggests that biocrude ratios of 15% and below are insufficient to induce visible changes in gasoline quality, at least under the operations conditions used in this experiment.

Conversely, Figure 13 reveals certain variations in FCC gasoline composition with the CTO ratio at 4 g/g. Relative to Figure 12 (CTO ratio of 10 g/g), the major difference is a widespread rise in olefins (21.0–23.2 wt %) and reduced levels of aromatics (44.4–48.8 wt %). Increasing the biocrude ratio in the feed under such conditions (CTO ratio of 4 g/g)

apparently leads to more olefins and naphthenes in gasoline while bringing down aromatics. This shift in gasoline composition can be linked to processing severity and, consequently, overall conversion in the FCC reactor. As discussed in Figure 4, increasing the CTO ratio from 4 to 10 g/g makes conversion go up from 62.3–66.3 to 71.1–73.9%, depending on the feedstock. It was also noted from the gasoline yield profiles (Figure 5) that around the 70–72% conversion mark gasoline yield tended to peak for all feedstocks, indicating the complete depletion of gasoline precursors in the feed. This suggests that gasoline composition evolves as a function of conversion until it reaches some form of equilibrium when gasoline yield peaks. On comparing Figures 12 and 13, the most visible part of this change in gasoline composition as conversion increases is the rise in aromatics, with a parallel fall in olefins. This rise in aromatics in gasoline is attributed to the conversion of monoaromatics into derivatives of benzene with a low degree of alkylation.

3.4. Biogenic Carbon Analysis. Table 3 reports the biogenic carbon test results for the three biocrude blends and

Table 3. Biogenic Carbon Analysis of the Biocrude Blends and Selected FCC Liquid Products^b

property	5% blend	10% blend	15% blend
biogenic carbon in FCC feed (%)	5	9	14
FCC liquid product yield ^a (wt %)	78.5	79.1	78.9
biogenic carbon in FCC liquid product (%)	5	10	15

^aTotal liquid product yield at a CTO ratio of 6 g/g. ^bNote: FCC, fluid catalytic cracking.

their corresponding total liquid products generated at a CTO ratio of 6 g/g. Biogenic carbon results indicate the percentage of biogenic carbon relative to the total amount of carbon in the sample. For the biocrude blends, it is noted that their biogenic carbon content is very close to the amount of HTL biocrude that was initially added to them before being subjected to the hydrotreating pretreatment step. This shows that nearly all of the biogenic carbon was retained in the liquid during hydrotreating.²⁷ The FCC liquid products, constituting 78.5–79.1 wt % of the total, exhibit the same trend suggesting that the majority of the biogenic carbon entering the FCC unit is preserved in the liquid products. However, to know the precise biogenic carbon balance, the coke and gas products must also be analyzed for biogenic carbon. This was not possible with the current test unit as it is not set up for recovering solid and gas byproducts. It is also noted that the scale of the test unit (~1 to 2 g feed input) was a limiting factor in producing large enough liquid product samples that could be physically distilled into gasoline, LCO, and HCO, for their subsequent biogenic carbon analysis. This is the reason why only the full-range liquid product recovered from the FCC tests was analyzed for biogenic carbon.

4. CONCLUSIONS

In this research, we have examined the impacts of coprocessing HTL biocrude through hydrotreating followed by FCC. The following are the conclusions of this study:

- Coprocessing the hydrotreated blends with 10% or more biocrude gave proportionally lower conversion levels in the FCC reactor with respect to the baseline petroleum

feed. This was attributed to a higher catalyst inhibition caused by the nitrogen and oxygen species in the biocrude blends.

- The 5% biocrude blend showed the highest selectivity toward gasoline at a given conversion, suggesting that its gasoline precursors were more reactive. Below 70% conversion, the 10 and 15% blends showed variations in gasoline selectivity with respect to the baseline feed, but at higher conversions, these deviations were minimum.
- LPG selectivity dropped for the biocrude blends. It is possible that HTL biocrude, being rich in aromatics with relatively short alkyl branches, is less likely to release C₃–C₄ fragments. This in part could also be the reason why the biocrude blends generated more dry gas.
- The biocrude blends yielded more LCO as a result of having more diaromatics.
- Owing to their polyaromatic and oxygen contents, the biocrude blends had a higher tendency to yield coke.
- Hydrocarbon type composition analysis revealed that the coprocessed gasoline fractions were virtually the same as the baseline gasoline product at high conversion (70–72%) in the FCC reactor.
- Biogenic carbon content in FCC total liquid products showed good correspondence with the amount of biocrude added to the feed, suggesting that most of the biogenic carbon is retained in the liquid product.

■ AUTHOR INFORMATION

Corresponding Author

Anton Alvarez-Majmutov – Natural Resources Canada, CanmetENERGY Devon, Alberta T9G 1A8, Canada; orcid.org/0000-0002-6958-3959; Phone: (+1) 780-987-8348; Email: anton.alvarez-majmutov@nrcan-rncan.gc.ca; Fax: (+1) 780-987-5349

Author

Yi Zhang – Natural Resources Canada, CanmetENERGY Devon, Devon, Alberta T9G 1A8, Canada

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.energyfuels.1c03152>

Notes

The authors declare no competing financial interest.

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