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Opportunities in Upgrading Biomass Crudes

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An unconventional crude from biomass (biocrude) has been processed to yield an hydrocarbon stream that is not only fully processable in conventional refineries but is already close to the specification of commercial fuels such as transportation diesel. The upgrading of biocrude was carried out with a combination of hydrotreatment and catalytic cracking, yielding middle distillate as main product.

1. Introduction

As the reserves of conventional crude are declining, new resources are developed to fulfil the increasing demand for transportation fuels. A number of synthetic crudes can be obtained from unconventional sources, such as extra-heavy crude oils or lignocellulosic biomass. These can be processed further in existing or upgraded refinery processes, taking advantage of the huge oil processing and distribution infrastructure available already. However, these crudes introduce new problems due to their composition.

Beyond most important environmental considerations, biofuels made from abundant lignocellulose (wood, grasses, etc.) are an opportunity for lowering the dependence on oil. It has been reported that in the United States alone 1 billion tonnes per year of lignocellulosic biomass would be available for its transformation into fuels. Yet economical transformation of lignocellulose into liquid fuels that can compete with petroleum-based products, has remained elusive. Cellulosic ethanol costs remain high due to the difficulty of deconstructing cellulose, either by chemical treatment or enzymatically. Also, the yield of alcohol is constrained since not all the biomass is used. Gasification followed by Fisher-Tropsch chemistry has been demonstrated to yield high quality product, but the process

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efficiency is about 50% and the associated capital costs remain very high.² Moreover, with smaller scale units, adapted to the biomass supply network, these costs increase even further. Fast pyrolysis is an efficient and cheap process to liquefy the biomass, but the quality of the liquid product obtained is too low for a straightforward application to transportation fuel. Upgrading through hydrotreatment has proved to be challenging due to the high oxygen content, and the process requires harsh operating conditions.³ Another simple technology that treats the whole of the lignocellulose is thermal hydrotreatment. In an aqueous medium when water is brought near its critical point (330-380°C, 200-300 bar), the lignocellulose breaks apart yielding a liquid and some gas (essentially CO₂ with only very minor amounts of H₂, CO and CH₄). Compared to pyrolysis oil, this liquid is of higher molecular weight and stable with a substantially lower oxygen content that makes upgrading much easier.⁴ As a result, the energetic content of the oil phase from hydrothermal treatment was reported in the range of 30-35 MJ/kg for a wide range of organic feeds⁵ as compared to the energetic content of pyrolysis oil, often in the range of 15-20 MJ/kg depending on the water content.⁶

In the present manuscript the upgrading of these unconventional (bio)crudes has been studied using processes that are well-known to the refiner or that can be directly derived from such processes. In this way it should be possible to treat the biocrude from hydrothermal treatment in the existing units of oil refineries, preferably mixed with the regular oil being processed.

2. Biocrude from hydrothermal liquefaction

2.1. Processing scheme and preparation of the biocrude supplied for the study

A multistep process was implemented to convert pine woodchips into fuels. The complete processing scheme is presented in Figure 1. We will describe in this section the steps that allowed producing the biocrude, which was supplied by Licella, and was further used in this study to explore upgrading options (catalytic cracking and hydrotreatment).

In the first step, Pine woodchips were processed hydrothermally in the presence of a catalyst, yielding a raw biocrude. One of the hurdles of such process development is the low productivity associated with batch treatment. Thus, a reactor allowing continuous treatment at 10,000 tonnes per year nameplate capacity was developed.7 The lignocellulose (e.g. pine woodchips) is reduced in particle size to suit the type of slurry pump being used. In these experiments the feedstock was reduced to about 500 microns diameter, however particle diameters of up to 2 mm have successfully been employed with the same pump and reactor configuration. The lignocellulose is suspended in water, and raised to the operating reaction temperature by a combination of electrical heating, heat exchangers and supercritical steam injection. The slurry is pumped into a vertically oriented, serpentine tubular reactor.8 Operating conditions are close to the critical point of water, optimally sub-critical in the 330-350°C temperature range and 200-250 bar.9 The

residence time in the reactor is typically around 20-30 minutes for woody biomass. At this stage the processing stream is an oil-water emulsion that contains a small amount of solid material, i.e. mostly ash from the feedstock. In the next step the stream is partially cooled and then directly flashed at the output of the high-pressure hydrothermal reactor, splitting the emulsion and ensuring a rapid and efficient separation of oily products and water phase. Catalyst and a number of water-soluble organics are removed with the water phase. These include products such as small ketones, acids and phenols that may be recovered from the aqueous stream for further valorization. On a dry basis the oily phase recovered may represent about 30-35 wt% of the dry biomass fed to the hydrothermal reactor. This now already dewatered oil is further distilled in order to remove the heaviest part, constituted of a material that tends to transform into char when exposed to temperature above 350°C. This heavy fraction represents 20-30% of raw biocrude, depending on the hydrothermal processing conditions.

Due to its characteristics, the resulting biocrude is not straightforwardly suitable for use as transportation fuel, so a final upgrading step is necessary. For that purpose we have studied two options. The simplest one is to mix the biocrude with Vacuum Gas Oil (VGO) and crack the mixture in a Fluid Catalytic Cracking Unit (Figure 1). A second option considers hydrotreat first the biocrude, which yields a number of distillate range products and then crack the remaining heavy fraction in a fluidized catalytic cracking (FCC) unit.

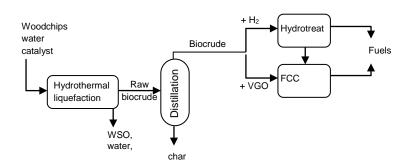


Figure 1. Two steps process for the preparation of biocrude and biocrude upgrading options.

2.2. Experimental

2.2.1. Biocrude characterization

The biocrude obtained after flash separation and distillation was extensively characterized. Elemental analysis (CHNS, EuroEA, Eurovector) showed a nitrogen content of 0.2%, no detectable sulphur (<0.1%) and a hydrogen to carbon (H/C) molar ratio of 1.36 (Table S1). We assumed that biocrude distillate did not contain ash, so that oxygen content was determined as difference from CHNS analysis. By this method, an oxygen content of around 12% was calculated. This product quality is much better than common pyrolysis oil, where oxygen contents as high as 40% with H/C molar ratio close to 1.0 are commonly found. The biocrude oxygen content and H/C ratio are indeed not too far from those of the

triglycerides present in plant oils or animal fats that are currently commercially hydrogenated. Simulated Distillation (SIMDIS) following ASTM-2887 guidelines of this oily product was also performed. Although SIMDIS data of oxygen-containing streams cannot be compared directly with those of pure hydrocarbon streams, since the removal of oxygen will result in a shift to lower boiling temperatures, it nevertheless gives an upper limit of the boiling point ranges in the sample. In our case this indicates that the biocrude is at least similar to a petroleum-based diesel stream, with 60 wt% of the sample having a boiling point between 216 and 359°C (diesel-range), 20 wt% below (gasoline-range) and 20 wt% above (bottoms-range) these limits. Consistent with the above discussion, it has to be noted that compared to a petroleum-based Vacuum Gas Oil, biocrude's heaviest components, as detected by chromatography, are significantly lighter than the heavy end tail detected in VGO SIMDIS chromatogram (Figure S1).

2.2.2. Catalysts characterization

A commercial NiMo supported on alumina was used as hydrotreating catalyst and its general properties are summarized in Table 1. Surface area properties were obtained through nitrogen adsorption on a Micromeritics ASAP2420 instrument. Ni and Mo content was obtained by Inductively Coupled Plasma (ICP) technique on a Varian 715-ES instrument. Unit Cell Size and zeolite content were determined from powder X-ray diffraction pattern (CubixPro, PANalytical). Zeolite content is given as compared with a CBV100 zeolite sample taken as reference. The hydrotreatment catalyst was used without further treatment and sulphided in-situ during the start-up of the experimental runs. The catalytic cracking catalyst was a commercial grade zeolite catalyst containing 3wt% Rare Earth. It was steam deactivated at 816°C for 4 hours with 100% steam and its main properties are summarized in Table 2.

Table 1. Hydrotreatment catalyst properties

| Catalyst | NiMo |
|-------------------------|------|
| BET (m ² /g) | 200 |
| Pore Volume (cm³/g) | 0.41 |
| NiO (wt%) | 23 |
| MoO ₃ (wt%) | 3 |

Table 2. Catalytic Cracking catalyst main properties after steam deactivation

| te 2. eatary the cracking eatary st main properti | ie zi catalytic cracking catalyst main properties after steam acadivation | | | |
|---|---|--|--|--|
| Rare Earth content (wt%) | 3.0 | | | |
| BET (m ² /g) | 144 | | | |
| Micropore volume | 0.06 | | | |
| UCS (Å) | 24.30 | | | |
| zeolite content (DRX, wt%) | 11 | | | |

2.2.3. Hydrotreating and cracking units

The hydrotreating unit (Figure S2) comprised a feeding tank, an HPLC pump, gas system (H_2 , H_2S/H_2 for pretreatment, N_2 purge), a fixed bed reactor, liquid collector, pressure control through a back-pressure-regulator (BPR) valve and gas exhaust. The feed tank was gently heated (60° C) and stirred to maintain the Biocrude Distillate at low viscosity. 4 grams of catalyst were mixed with Silicon Carbide (SiC) to adjust the total bed volume to 8 ml (approx. 6 grams). An additional 1 ml SiC was added on the top of the bed. The catalyst was crushed and sieved into 0.2 to 0.8 mm particles to avoid diffusion limitations. Once loaded, the catalyst was sulphided at 400°C with a stream of 10% H_2S in H_2 (120 ml/min) for at least 12 hours.

Then, reactor was set to operating temperature (350°C) and the system was pressurized with hydrogen at 40 bars. Feed injection started once the pressure was stabilized. The hydrogen feed rate was adjusted to 100 Nml/min, which represents 13.3 wt% of the total feed. As this is a large excess when compared to the amount of hydrogen consumed for gas oil hydro-desulphurisation (HDS) (below 1 wt%) or even hydrodeoxygenation (HDO) of Biocrude Distillate (3-6 wt % range), it was done to ensure that hydrogen partial pressure remains high at every point in the reactor. Weight Hourly Space Velocity was maintained at 0.5 h⁻¹ during the whole run.

Mass balances were performed at regular intervals. The liquids recovered were weighed and for each liquid sample at least one gas sample was analyzed online. Gas samples were taken downstream of the BPR valve. CO, CO₂ and C₁-C₆ gas concentrations were determined. The coke yield was considered very low when estimated from the mass balance (below 1%) and was confirmed by the analysis of coke on the catalyst. An aqueous phase formed a well-defined layer at the bottoms of the liquids, and could be easily extracted by pipetting. The remaining water content of the oily phase was determined by Karl-Fischer titration after extraction of the aqueous phase from the liquids and determined to be negligible. The remaining organic phase was analyzed by SIMDIS (ASTM-D-2887). Three cuts were determined from the boiling point curve to help for the discussion. Gasoline-range fraction grouped the components with boiling point below 216°C (as determined by SIMDIS) and diesel-range fraction the components having a boiling point between 216 and 359°C. Bottoms grouped the component boiling above 359°C. These cuts and the discussions referred to them, especially in the catalytic cracking part, must be understood strictly as SIMDIS cuts and not commercial fuels. Indeed, the SIMDIS of a commercial road diesel may show some gasoline and bottoms fractions. In catalytic cracking, diesel and bottoms fractions are often designed as Light Cycle Oil (LCO) and Heavy Cycle Oil (HCO) due to their aromatic nature. Some of the liquid products were also analyzed through GCxGC-MS technique, using a system configuration known as reverse GCxGC. Here, the first column (INNOWAX, 30m x 0.25mm x 0.25 μm) is polar, while the second one (DB5, 5m x 0. 25mm x 0.25 μ m) is apolar. A flow modulator was used, with a modulation period of 4.5 s. The oven temperature was maintained at 50°C for 5 minutes,

then ramped at 2°C/min ramp up to 250°C, followed by a plateau for 60 minutes. The second oven followed the first oven program with a 10°C offset. FID temperature was at 300°C, acquisition frequency 100Hz. MS acquisition frequency was set at 14 spectra/s in a mass range of 40–360 amu

Cracking was performed in a fixed-bed Micro Activity Test unit modified from ASTM-3907.10 Operating conditions were: 500°C reaction temperature, 30 seconds Time-On-Stream and a Catalyst-to-Oil ratio in the range of 2 to 5. These conditions were elected to maximize middle distillates yield. Liquids products were recovered in glass receivers and gases were recovered in a water burette or a gas bag when biocrude was present in the feed, as CO/CO₂ and some of the oxygenated products would have been lost in the water. Pressure during the test remained close to atmospheric. After the reaction, a 15 minutes stripping with nitrogen at 50 ml/min was performed. The catalyst was regenerated with air at 550°C for 3 hours. Gas and liquid samples were analyzed as described in the former paragraph. Nitrogen was used as internal standard to determine the total volume of gas recovered when using a gas bag. C₅⁺ components and oxygenates in the gas were fully quantified and their weight added to the gasoline fraction in the mass balance. When biocrude was present in the feed, experiments were duplicated and the water was extracted from the liquid product using methanol. The extract was then analyzed by Karl-Fisher titration to determine water content. The coke yield was determined by combustion and integration of the CO₂ signal in flue gas measured by infra-red spectroscopy (IR). The conversion was calculated as the sum of gas, gasoline, diesel and coke products. The mass balances performed were 95% or higher in all series.

2.3. Results and discussion

2.3.1. Direct catalytic cracking

Direct cracking of the Biocrude was performed, using either a pure feed or a blend with a standard Vacuum Gas Oil (VGO) containing 10 or 30 wt% of biocrude. This was then compared to the results achieved by cracking the VGO alone. Conversion in catalytic cracking is often defined by convention as the sum of gas, gasoline and coke products. However, in the present case, owing to the unconventional nature of the crude treated, we have preferred to define the conversion as the sum of gases, gasoline, diesel and coke products, sometimes referred as total conversion in conventional catalytic cracking. It should also be taken into consideration that diesel-range products are quite interesting at present. As can be seen in Figure 2, (total) conversion did not vary much with the incorporation of increasing amounts of biocrude in the VGO. Dry gas selectivity increased with the presence of biocrude, while LPG selectivity decreased. Gasoline selectivity decreases and diesel (Light Cycle Oil, LCO) selectivity increases with the increase of biocrude in the feed mix, with such an amplitude that by the traditional definition the conversion as the sum of gas, gasoline and coke would have decreased largely when biocrude is added. The result could then give the *misleading impression* that the biocrude

is very refractory to convert. Instead, the amount of (unwanted) bottoms remaining after cracking varies only slightly when biocrude is added. Finally coke selectivity increases with the presence of biocrude, as does coke-on-catalyst. This last point will strongly limit the direct processability of Biocrude in a Fluid Catalytic Cracking Unit (FCCU), as coke yield is determined by the thermal balance of the unit. Then an important increase in coke yield resulting from the incorporation of biocrude into the VGO feed will increase the temperature in the regenerator and consequently will result in a reduction of the catalyst to oil ratio in the FCCU, thus indirectly decreasing the conversion of the processed mixture. As a comparison, untreated pyrolysis oil also tends to produce increased coke yields. Coke yield increase is less pronounced when the oil is hydrotreated or obtained through catalytic pyrolysis. All these oils tend to yield as much as or more gasoline than the VGO used as standard This is a consequence of the pyrolysis oil composition, that includes highly oxygenated small molecules that ends as monoaromatics with few alkyl carbons, especially when ZSM5 is used in catalyst formulation. By the contrary, the present biocrude tends to form multi-ring aromatics that end in the diesel fraction as explained below.

The propylene to propane ratio increases with high levels of biocrude in VGO, as does the isobutene to iso-butane ratio. This implies that hydrogen transfer reactions are suppressed with higher levels of biocrude, which is a direct consequence of higher coke-on-catalyst. Also, the higher amounts of poly-aromatics generated in the cracking of the biocrude plays a role in catalyst deactivation. The analysis of the diesel fraction, the yield of which increased sharply with biocrude addition, revealed that it is very aromatic in nature (Table 3). Also, when biocrude was co-fed a significant amount of oxygenated compounds, essentially phenols and its derivates, were detected in the diesel range. This is in accordance with the composition of the biocrude, where NMR analysis revealed that oxygen is bound essentially in furanic and aromatic form. The aromaticity of the diesel fraction explains why such high yields of diesel could be maintained even at the higher catalyst-to-oil ratio (giving higher conversion), as these kind of aromatics crack only to a very limited extent to yield gasoline and gaseous fragments.

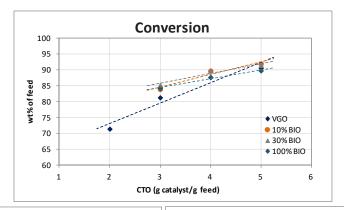
Table 3. Diesel yield and composition, CTO=5, increasing amount of distilled biocrude in VGO.

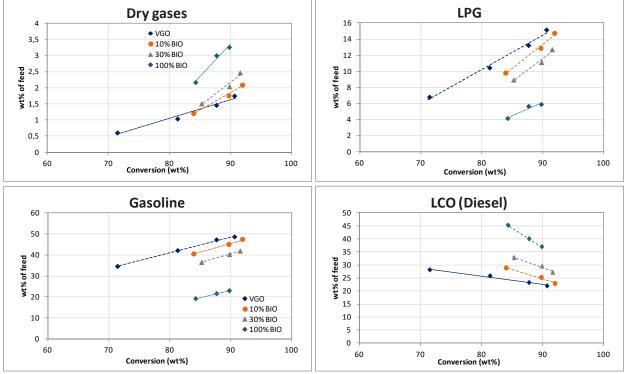
| % biocrude in VGO | 0 | 10 | 30 | 100 |
|-------------------|------|------|------|------|
| Diesel, wt% | 22.0 | 22.9 | 26.9 | 37.6 |
| Composition, wt% | | | | |
| Saturates | 15.9 | 11.7 | 9.3 | 2.1 |
| Mono-aromatics | 21.8 | 20.5 | 17.6 | 14.5 |
| Poly-aromatics | 62.1 | 63.9 | 63.1 | 53.8 |
| Oxygenates | 0.2 | 3.9 | 10.1 | 29.7 |

Independent of the biocrude content of the feed, oxygen was converted mainly into water, with a yield in the 40-60% range. CO and CO_2 were also produced, totalling less than

10 wt% of the feed oxygen, with more CO than CO_2 . This indicates that there are only few acids to decarboxylate in the feed. In fact, the oxygen balance implies that 30 to 50 wt% of the feed oxygen was still retained in the liquid products or the coke. The amount of oxygenates found in the diesel products is thus consistent with the former observations.

Therefore, the direct catalytic cracking of the biocrude, while being a straightforward and very cheap option, will then be limited to low amounts in co-processing with VGO, below 10 wt%. Nevertheless, an FCC unit in where 2-5 wt% of biocrude will be introduced together with a conventional feed coming from oil could be acceptable from the point of view of the FCCU stability. Note that a 5% share in a FCC unit (FCCU) of 30,000 bpd capacity (roughly 1.5 million tons per year) still represent around 200 tons per day of biocrude to be treated.





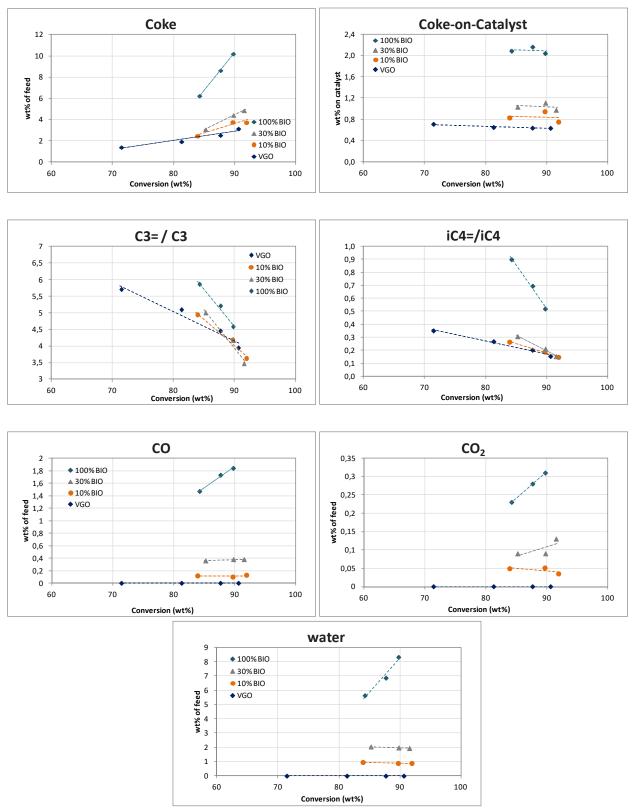


Figure 2. Catalytic cracking of Biocrude, VGO and their mixture, at 500°C, TOS=30s and Catalyt-to-oil ration in the 2-5 range. Conversion, selectivity towards main products, coke-on-catalyst and olefins to paraffins ratios of interest.

2.3.2. Hydroprocessing followed by bottoms cracking

In an alternative approach the biocrude was hydrotreated with a commercial desulphuration-deoxygenation catalyst in order to improve its quality. While this catalyst is primarily optimized for use with petroleum feedstocks, it also presents an appreciable activity towards deoxygenation. The hydrotreating operating were soft, with a total pressure of 40 bars, a temperature of 350°C and a WHSV of 0.5 h⁻¹. Similar hydrotreating conditions have been employed successfully with feeds such as plant oils or tall oil. 16,17

Hydrotreating results are reported in Table 4. In spite of using a treatment pressure in the lower range compared to standard diesel hydrotreatment, deoxygenation of the biocrude was nearly complete, with a recovered water yield very similar to the oxygen content in the feed. Elemental analysis of the recovered oil (i.e. separated from the water phase) confirmed that the oxygen content was below 1 wt%. Others biocrudes from hydrothermal treatment were also hydroprocessed to full deoxygenation, but under much more severe operating conditions. 18,19

The amount of CO and CO₂ in the gas remained very low, and contained less than 5 wt% of the oxygen in the feed. Oxygen was thus removed essentially through a hydrogenationdehydration mechanism. Gas yield was significantly higher than what is commonly found for hydrocarbon processing, in which gas yield is generally below 1 wt%. The obtained oil contains more gasoline and fewer bottoms than the feed. In particular, the higher boiling point fraction (approximately 20 wt% in the feed boiling above 359°C) was reduced by half in the oil produced. The heavy fraction may be reduced further higher pressure processing. The density of the oil product was found to be high compared with the specifications for a road diesel, in spite of a significant light fraction in the product (30% gasoline-range products). The composition determined by GCxGC for the hydroprocessed oil showed a significant amount of aromatics and poly-aromatics (PAH). Some oxygenated compounds, essentially substituted phenols, were also detected and totalled approximately 1.5 wt% of the oil sample with respect to the feed. The oxygen content of the oil resulting from the presence of these components, in the 0.2 to 0.4 wt% range, is in accordance with Elemental Analysis observations. These compounds were lumped with PAH in Table 4. The alkanes and naphthenes fraction (Saturates) represented more than 40% of the oil, which density remained surprisingly high in view of this composition. Indeed, GCxGC chromatogram revealed that the Saturate fraction included a large amount of poly-cyclic naphthenic products of the decalin family, which have a substantially higher density than the corresponding paraffins with the same carbon number (decane density is 0.730 g/cm³ while decalin – decahydronaphthalene – density is 0.896 g/cm³). Furthermore, the aromatic fraction contained numerous isomers of the tetralin family, which are also denser than the corresponding decalins. It may then be interesting to further treat these streams with a dearomatization/ring opening catalyst to lower product density. Little pre-treatment would be needed as the hydroprocessed product is sulphur and nitrogen free and has only very low, if any, oxygen remaining.

Table 4. Operating conditions, yields and hydrocarbon product characteristics for the hydroprocessing of Biocrude.

| Operating conditions | | | | |
|-------------------------------|-------|--|--|--|
| Catalyst | NiMo | | | |
| P (bars) | 40 | | | |
| WHSV (h ⁻¹) | 0.5 | | | |
| Reactor temperature (°C) | 350 | | | |
| Yields, wt% | | | | |
| Gas | 1.9 | | | |
| Liquids: ibp-216°C | 28.9 | | | |
| 216-359°C | 49.8 | | | |
| 359°C-fbp | 8.1 | | | |
| water | 11.2 | | | |
| Hydroprocessed oil properties | | | | |
| density (g/cm³) | 0.916 | | | |
| Saturates (wt%) | 42.0 | | | |
| Mono-aromatics (wt%) | 44.1 | | | |
| PAH & oxygenates (wt%) | 13.9 | | | |

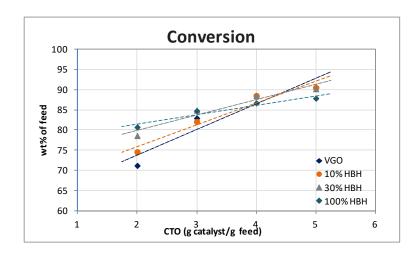
The oil product from hydroprocessing at 40 bars was further fractionated using equipment and operating conditions similar to those described in the ASTM-D-1160 method. The operation yielded a gasoline-range fraction (30 wt%), a diesel-range fraction (54 wt%) and a heavy fraction (16 wt%). Note that the cut point between diesel-range and heavy fraction was lowered at 300°C in this distillation, so that the yield of heavies increased compared to standard cut point (340-360°C) used in refining operations. This Hydrotreated Biocrude Heavies (HBH) fraction had a density of 0.995 g/cm³, and was further processed by catalytic cracking. The same protocol as in section 2.3.1 was used, that is mixing with a VGO at 10 and 30 wt% level as well as comparing with 100% HBH cracking.

Following the same reasoning as applied to the original biocrude, we report here the selectivity calculated for a conversion defined as the sum of gases, gasoline, LCO (diesel) and coke yields. The (total) conversion of HBH offers some similarity with that of the biocrude in the sense that the conversion does not change much with the incorporation of a biomass-based stream into VGO, and that the selectivity largely shifts from gasoline to diesel range products. Yet the large difference lies in dry gas and coke selectivity, which are now similar for VGO and HBH. Thus, contrary to biocrude, HBH could be processed even at high blending levels in VGO, with no penalty in conversion. LPG selectivity decreased slightly with the incorporation of HBH, and the olefinicity of the LPG decreased, indicating that hydrogen transfer took place with HBH to a greater extent. This is due to the nature of HBH, which contains a significant amount of hydro-aromatics. Indeed, these compounds could be detected through GCxGC-MS analysis, as it is shown in Figure S3. Apart from some linear paraffins, the main components of the highlighted groups of peaks in this figure

included structures with 3 fused rings of the anthracene or phenanthrene family with varying degree of saturations, from saturated 3 rings naphthenes to tri-aromatics. 3-ring saturated systems may crack yielding gas and gasoline components, but hydro-aromatics will be prone to hydrogen transfer, yielding poly-aromatics with 2 or 3 fused aromatic rings that belong to the LCO fraction.²⁰ The composition of diesel fraction in the cracked liquid in Table 5, determined by GCxGC, shows very clearly an increase of the poly-aromatics when increasing the amount of biocrude in the feed. The poly-aromatics formed after hydrogen transfer will accumulate mainly in the LCO fraction, which partially explains the higher selectivity to this fraction at the expense of gasoline and gases. As the oxygen content in HBH was very low, no CO/CO₂ or water could be detected in the products. Traces of phenolic and benzofuranic compounds could be observed in the diesel fraction, but always with a total amount below 0.5 wt% and they were grouped with the poly-aromatics fraction. Taking into account the amount of oxygen in phenol-like compounds, we can assume that the cracked diesel has a content of oxygen below 0.1 wt%.

Table 5. Diesel yield and composition with increasing amounts of biocrude. Catalytic cracking of HBH, CTO=4, 500°C, TOS=30s

| % HBH in feed | 0 | 10 | 30 | 100 |
|------------------|------|------|------|------|
| Diesel, wt% | 24.7 | 25.9 | 31.0 | 43.2 |
| Composition, wt% | | | | |
| Saturates | 19.0 | 16.7 | 13.2 | 4.3 |
| Mono-aromatics | 24.2 | 23.0 | 21.3 | 17.0 |
| Poly-aromatics | 56.8 | 60.3 | 65.6 | 78.7 |



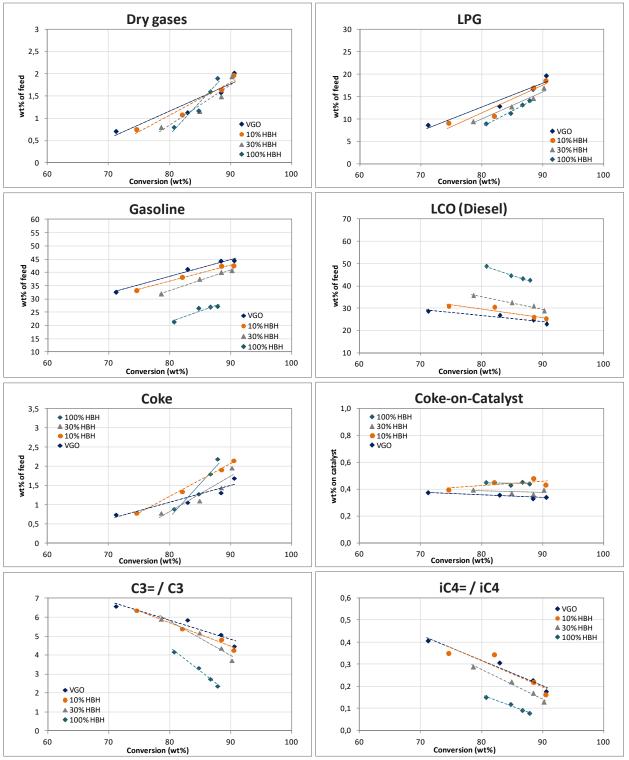


Figure 3. Catalytic cracking of Hydrotreated Biocrude Heavies, VGO and their mixtures at 500°C, TOS=30s and Catalytto-oil ration in the 2-5 range. Conversion, selectivity towards main products, coke-on-catalyst and olefins to paraffins ratios of interest

Conclusions

Biocrudes obtained from lignocellulose through a hydrothermal treatment have been upgraded so that they can be further refined using the existing infrastructure (drop-in replacement). Amounts of biocrude below 10 wt% could be directly fed to the catalytic cracker. A better option for higher blends of Biocrude is processing through soft or mild hydroprocessing, yielding a diesel-range stream free of sulphur and very low in oxygen that can readily be refined with the straight-run gasoil, or may be directly used as diesel pool additive. The heavy ends from hydrotreatment may also be sent to an FCC unit.

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