

Document downloaded from:

<http://hdl.handle.net/10251/122257>

This paper must be cited as:

Sauvanaud, LL.; Mathieu, Y.; Corma Canós, A.; Humphreys, L.; Rowlands, W.; Maschmeyer, T. (2018). Co-processing of lignocellulosic biocrude with petroleum gas oils. *Applied Catalysis A General*. 551:139-145. <https://doi.org/10.1016/j.apcata.2017.09.029>



The final publication is available at

<http://doi.org/10.1016/j.apcata.2017.09.029>

Copyright Elsevier

Additional Information

Co-Processing of Lignocellulosic Biocrude with Petroleum Gas Oils

L. Sauvanaud,^[a] Y. Mathieu,^[a] A. Corma^[a], L. Humphreys,^[b] W. Rowlands^[b] and T. Maschmeyer,^[c]

[a] Dr. L. Sauvanaud, Dr. Y. Mathieu, Prof. A. Corma
Instituto de Tecnología Química,
Universitat Politècnica de València – Consejo superior de Investigaciones
Científicas (UPV-CSIC)
Avda. dels Tarongers, s/n 46022 Valencia (Spain)
E-mail: acorma@itq.upv.es

[b] Dr. L. Humphreys, Dr. W. Rowlands
Licella Pty. Ltd.
Level 7 140 Arthur St
North Sydney NSW 2060 Australia

[c] Prof. T. Maschmeyer
School of Chemistry
The University of Sydney
NSW 2006 Australia

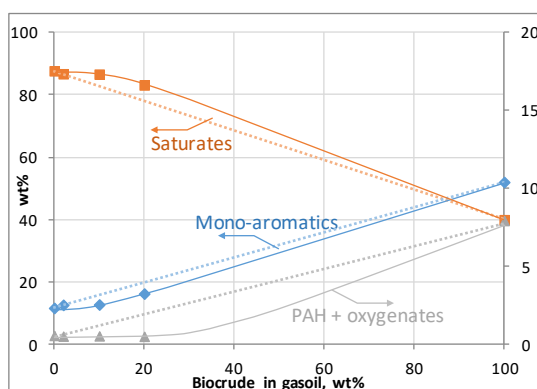
Abstract

A biocrude was obtained via the catalytic hydrothermal treatment of lignocellulosic biomass. This was further co-hydroprocessed with Straight Run Gas Oil (SRGO) under desulphurization conditions. Amounts of biocrude of up to 20 wt% could be co-processed, while maintaining a diesel stream density within the specifications contained in the road diesel regulation EN 590. The changes in the diesel properties associated with an increasing amount of biocrude were not a simple linear function of biocrude content. Rather, some positive correlations seem to exist between biocrude and SRGO at low biocrude contents, possibly due to intramolecular hydrogen transfer, yielding a diesel stream with a better quality than would be obtained from simply mixing hydrotreated pure streams in a 80% to 20% ratio.

Keywords

Biocrude, lignocellulose, diesel, refining

Graphical Abstract



Highlights

- A biocrude was co-processed with Straight Run Gas Oil under typical hydrotreatment conditions
- The inclusion of up to 20 wt% of biocrude yielded an on-spec diesel stream
- The biocrude performed better than Light Cycle Oil in mixture with Straight Run Gas Oil

1. Introduction

The demand for liquid transportation fuels is expected to remain very strong in the decades to come, as it is likely that the increase in ICE (internal combustion engine) efficiency and the development of electric propulsion will be balanced by nearly a doubling of the car fleet in the next 20 years.¹ To fulfill the associated demand for liquid fuel, while striving to decrease CO₂ emissions, an avenue is provided by the introduction of unconventional resources such as biomass-derived fuels. First generation biofuels from edible sugars or oils have limited environmental benefit and supply. Meanwhile, large amounts of lignocellulosic biomass in the form of wood, leftovers or dedicated energy crops are available, with an estimated 1 billion tonnes per year for the United States alone.² Although insufficient to replace all of the liquid fuel currently produced, it certainly has the potential to meet a part of the demand. Several routes for the transformation of lignocellulose into liquid fuels are being industrialized, while attempting to compete with petroleum-based fuels on an unsubsidized or narrowly subsidized basis. Lignocellulosic materials may be deconstructed into their components (cellulose, hemicellulose and lignin) by chemical or enzymatic treatment and the sugars fermented into alcohols. The main obstacles to low cost cellulosic alcohols remain the pretreatment cost, and the constrained yield of alcohol per ton of dry biomass due to the presence of impurities in the sugar stream and the inability to ferment lignin.³ Hemicellulose can be converted into high quality diesel via the Sylvan process.⁴ The whole lignocellulose may also be gasified, and the syngas processed through Fisher-Tropsch systems to yield a high quality hydrocarbon stream. The process was demonstrated, but the process efficiency is about 50% and the associated capital costs remain very high.⁵ Moreover, with smaller scale units, adapted to the biomass supply network, these costs increase even further. Another process that takes advantage of processing the whole biomass is fast pyrolysis. While the process is cheap and the amount of energy of the dry biomass retained in the liquid biocrude can be above 60%, said biocrude quality 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.⁶ Catalytic pyrolysis has been explored attempting to improve bio-oil quality while reducing mass yield through in-situ deoxygenation.⁷ Another simple technology that treats the whole of the lignocellulose is hydrothermal treatment. 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.⁹ 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 feeds¹⁰ as compared to the energetic content of pyrolysis oil, often in the range of 15-20 MJ/kg depending on the water content.¹¹ However, the biocrude also still needs to be refined further to meet transportation fuel requirements. As an oxygenated, hydrogen-deficient feed, the best upgrading process is through hydrotreatment. It would be an advantage to process these biocrudes within existing refineries, taking advantage of the huge oil processing and distribution infrastructure available already. It has to be also taken into account that a world-scale biomass operation may process up to one million ton of dry biomass per year. With a very conservative mass yield of 25 wt% of low oxygen biocrude this translates into approximately 4000 barrels per day of biocrude, that is between 10 and 20 wt%

of the throughput of a large scale gas oil hydrotreater. It is then sound to test co-processing of biocrude with gas oil in mixtures up to 20 wt%. Higher blend ratios would benefit from separate processing under optimized operating conditions and catalyst. Previous attempts to hydrotreat biocrudes from hydrothermal treatment required low space velocities in order to achieve full deoxygenation.^{12,13} Instead, we have explored the co-processing of biocrudes from hydrothermal treatment in gasoil hydrotreating units with limited amounts of biocrude under common refining conditions, using common refinery catalysts.

2. Materials and methods

2.1. Biocrude preparation and characterization

The biocrude was taken from a 10,000 slurry tonnes per year capacity demonstration unit in which Pine woodchips, after comminution, were processed hydrothermally in the presence of a catalyst in a tubular reactor, yielding a raw biocrude. The woodchips are prepared by grinding to a suitable particle size for slurry pumping, 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.¹⁴ Operating conditions are close to the critical point of water, typically sub-critical in the 330-350°C temperature range and 200-250 bar.¹⁵ 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 and contains a small amount of solid material, 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, separating the producer gas and providing a means of heat recovery. The biocrude is typically denser than water and insoluble in water, ensuring a rapid and efficient separation of oily products and water phase. The 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 accounts for up to around 35 wt% of the dry biomass reacted. This now already dewatered oil is further distilled to remove metals and the heaviest part of the biocrude (15-30 wt%) and to avoid the formation of coke upon heating at 350°C or more in subsequent upgrading processes.

Elemental Analysis of the biocrude obtained after flash separation and distillation showed an oxygen content of around 12%, a low nitrogen content of 0.2%, no detectable sulphur (<0.1%) and a carbon to hydrogen molar ratio of 1.36. This biocrude is of much higher quality than thermal 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 C/H 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) 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 temperatures, it nevertheless gives an upper limit of the boiling point ranges in the sample. In our case this indicates that the biocrude would be similar to a petroleum-based diesel stream, with 20 wt% boiling above 360°C.

2.2. Hydrotreating catalyst physicochemical properties

A commercial sample of a NiMo supported on alumina was used as the hydrotreating catalyst. Its general properties are summarized in Table 1. While this catalyst is optimized for Gas Oil (GO) hydrotreating and hydrodesulphuration, it is not particularly optimized for hydrodeoxygenation, but is thought to have enough activity for treating blends with low amounts of biocrude without modifying operating conditions for GO treatment.

As the boiling point of the biocrude heaviest components lies in the range of Vacuum Gas Oil (VGO), the catalyst was shaped into 0.2 to 0.8 mm particles to avoid diffusion limitation, as is commonly done for laboratory VGO hydrocracking.¹⁶ Before the run, the catalyst was sulphided *in-situ* at 400°C with a stream of 10% H₂S in H₂ (120 ml/min) for at least 12 hours.

Table 1. Hydrotreatment catalyst properties

Catalyst	NiMo
BET (m ² /g)	200
Pore Volume (cm ³ /g)	0.41
NiO (wt%)	5
MoO ₃ (wt%)	22

2.3. Hydrotreating set-up

A fixed bed was used for the processing of Straight Run Gas Oil (SRGO) and its various mixtures with Biocrude (BIO) and /or Light Cycle Oil (LCO) from Fluid Catalytic Cracking. The liquid mixture is fed from a heated, stirred tank (60°C) through an HPLC pump into the reactor, where it contacts with the catalyst in the presence of hydrogen. Liquids are collected in a condenser at room temperature below the reactor, while the non-condensed gases are released through a Back Pressure Regulator (BPR) valve and can be analyzed online by a gas chromatograph. 4 grams of catalyst were mixed with Silicon Carbide (CSi) to adjust the total bed volume to 8 ml (9mm internal diameter, 130 mm length) in order to attain bed isothermicity and avoid coke plugging. CSi layers of around 1 cm thickness are also added above and below the catalytic bed to act as preheater and minimize heat losses from the bed. After sulphidation of the catalyst, the reactor was set to operating temperature and the system was pressurized with hydrogen. Once the pressure was stabilized, feed injection was started. Feed rate was 4g/h (Weight Hourly Space velocity 1 h⁻¹) and the hydrogen flow rate was maintained at 100 Nml/min, which represents 13.3 wt% of the liquid feed. As hydro-desulphurisation (HDS) usually consumes less than 1 wt% and hydrodeoxygenation (HDO) of Biocrude is expected to consume between 3 and 6 wt % based on the oxygen content of the feed, this large excess will ensure that hydrogen partial pressure remain high at every point in the reactor. After the system settles down for a 2-4 hour period, mass balances were performed at regular intervals.

2.4. Mass balance and product analysis

For each mass balance, the liquids recovered from the separator were weighed. At least one gas analysis was carried out during the period. Gas samples were taken downstream of the BPR valve. CO, CO₂ and C₁-C₆ gas concentrations were determined. Coke yield was disregarded for the mass balance for being very low (<0.2 wt% of the liquid fed), as confirmed later by the analysis of coke on the catalyst. When Biocrude was present in the feed, an aqueous phase formed a well-defined layer at the bottoms of the liquids, and could be easily extracted by pipetting. Water content was determined by Karl-Fischer Titration, such as to be able to calculate overall water yield. The oily phase was found to be substantially free of water. This phase was analyzed by SIMDIS (ASTM-D-2887). Cut points were set at 216°C for light distillate and at 359°C for the middle distillate fraction. Some of the liquid products were also analyzed with the 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 μm) 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. The FID temperature was at 300°C, the acquisition frequency was 100Hz. The MS acquisition frequency was set at 14 spectra/s in a mass range of 40–360 amu. The compounds detected were classified into the following groups:

- Saturates, including paraffins, naphthenes, olefins (if any) and also multi-ring saturated compounds of the decalin (octahydrophenanthrene, two rings) and 18-norabietane (three-ring) families.
- Monoaromatics, including hydroaromatics with one aromatic ring such as tetrahydronaphthalene and octahydroanthracene families
- Polyaromatics with at least two aromatics rings, including naphthalenes, anthracenes, fluorenes families.
- Oxygenated compounds, mainly of the phenols and guaiacol families.

3. Results and discussion

3.1. Co-processing of Biocrude with SRGO

A Straight Run Gas Oil was used as a reference feedstock to be treated under typical hydrotreatment conditions at 70 bars, 350°C and a space velocity of 1 h⁻¹, in the presence of a commercial NiMo/alumina catalyst. Then, blends with increasing amounts of biocrude in SRGO (2, 10 and 20 wt%) were processed and the results compared with those of processing 100% SRGO (base case) as well as with those from 100% Biocrude under the very same conditions. Results were reported after 50 hours on stream for all the runs.

The inclusion of Biocrude in the base stock led to an increase in the gas yield and water yield, proportional to the amount of Biocrude in the mix as shown in Table 2. The water yield was close to what is expected based on the oxygen content in the mix (associated with the biocrude stream), indicating that most of the oxygen in the feed was effectively removed, essentially through hydrodeoxygenation reactions. CO or CO₂ remained below detection limits with blends up to 20 wt% of biocrude. Yields of 0.2 wt% CO and 0.5 wt% were detected when processing 100% biocrude. Detailed gas yield (Figure 1) showed a noticeable increase in methane and propane when processing a SRGO-Biocrude mixture, while the change in ethane and butanes yields was moderate. While the yield increases are approximately proportional to the amount of biocrude in the mixture, it is not the case for propane, where a sharp decline from the initial yield is observed. Some deactivation may happen with large amounts of biocrude, yet the catalyst is still able to convert most of the oxygen after 50 hours on stream.

The hydroprocessed oil recovered showed a slight increase in light fraction (boiling point below 216°C) and a slight decrease in the middle and heavy fractions with the increase of biocrude in the feed, in accordance with the distillation curve found when processing 100% biocrude. Note, that in spite of the observed shifts, the whole hydroprocessed oil distillation properties still fully match the distillation specifications for road diesel such as those found in regulation EN 590. Interestingly, although the oil had a lower boiling point range, its density increased. Mixtures with up to 20 wt% biocrude yielded oils that still laid within road diesel specifications (0.82-0.845 g/cm³), while the oil obtained from 100% biocrude processing was fractionally denser, just above 0.900 g/cm³. This is closely related to changes in oil composition, which was examined in detail with GCxGC methods. Indeed, the inclusion of biocrude in the feedstock led to a decrease in saturates and an increase in aromatics as defined in section 2.4. It has to be noted, however, that the compositional change was not linear with the biocrude content in the hydroprocessed mixture, as shown in Figure 2. Indeed, the hydroprocessed oil from the mixture showed a larger amount of saturates and a lower amount of aromatics than could be expected by mixing the hydroprocessed output from the two feedstocks separately. Very interestingly, the amount of polynuclear aromatics and oxygenates remained very low and is similar to that obtained from the base stock with a biocrude content of up to 20 wt%. This may result from some synergy between the two feeds, with the SRGO acting as hydrogen donor for the biocrude. It may be also explained by a partial deactivation of the catalyst when contacting with biocrude only, leading to a lesser saturation of aromatic cores.

The very low amount of oxygenated products indicate that the oxygen content of the hydroprocessed oil will be very low, indeed it remained below the detection limits of Elemental Analysis (≤ 0.2 wt%). Meanwhile, the oil from processing 100 % biocrude showed a 0.7 wt% oxygen content on Elemental Analysis. Most of the oxygenated components detected in the hydroprocessed oil were of the methoxybenzene, phenol and guaiacol families, their relative quantities and oxygen content being consistent with the observed overall composition of 0.7 wt% oxygen. Previous investigators found that such low oxygen contents in the hydrotreated products could only be obtained **under more severe operating conditions when treating unmixed biocrude, with fully deoxygenated oil from 100% biocrude requiring space velocities of 0.1 h⁻¹ at temperatures of 350 to above 400°C and pressures above 120 bars.**^{12,13} Similar results were also reported by Shell.¹⁷ In making this comparison it should be noted that the biocrude was here distilled before hydrotreating, removing the heaviest part, which is significantly harder

to treat than the lighter fraction of biocrude. While the distillation step reduces the proportion of the biocrude oil that can be processed by conventional hydrotreating, we believe this may be a more efficient strategy for co-processing biocrude in the refinery, when the biocrude stream represents only a small fraction of the gasoil stream. The resid from the distillation can be expected to find application in other areas, for example it has shown considerable promise in testing as a renewable bitumen replacement in asphalt concrete. Gathering enough biocrude for setting up a stand-alone, dedicated unit operating with specialized catalyst with most likely harsher conditions than employed here to treat a larger portion of the biocrude would likely only be economical, unless strongly incentivized, by combining the output of several large lignocellulose liquefaction plants, representing a biomass usage of several million tons per year covering disperse locations. The option presented here, however, gives a cheap, straightforward output for starting lignocellulose to fuels business before multiplication of hydrothermal plants allows enough output for entire, dedicated biorefineries to be built.

Table 2. Yields for the processing of SRGO-Biocrude-LCO mixtures. Reaction temperature 350°C, 70 bars, 1h⁻¹.

Run	Feed composition ^a		Yields			Oil properties				Oil composition wt%			
	Biocrude, wt%	LCO feed, wt%	Gases	oil	water	Boiling point (°C)			density @ 20°C	Sat.	Mono Ar	PNA	Oxygenates
						<216	216-359	>359					
1 ^b	0	0	0.3	100	0	12.2	79.0	8.7	0.817	87.7	11.7	0.5	0.0
2	2	0	0.3	100	0	15.2	77.0	7.8	0.821	86.8	12.7	0.4	0.1
3	10	0	0.5	99	1	15.1	77.1	7.8	0.826	86.7	12.8	0.5	0.1
4 ^b	20	0	0.7	97	2	18.0	74.8	7.1	0.831	83.2	16.3	0.5	0.1
5 ^b	100	0	2.0	87	11	29.9	65.4	4.4	0.906	40.0	52.1	4.8	3.1
6	10	10	0.4	99	1	18.0	75.6	6.4	0.835	80.7	18.6	0.6	0.1
7 ^b	0	20	0.2	100	0	17.0	76.0	7.0	0.836	78.5	20.6	0.8	0.0

^aThe remaining of the feed mixture is Straight Run Gas Oil; ^b adapted from reference 9c

Figure 1. Detailed gas composition with several content of biocrude in the feeding mixture. Reaction temperature 350°C, 70 bars, 1 h⁻¹.

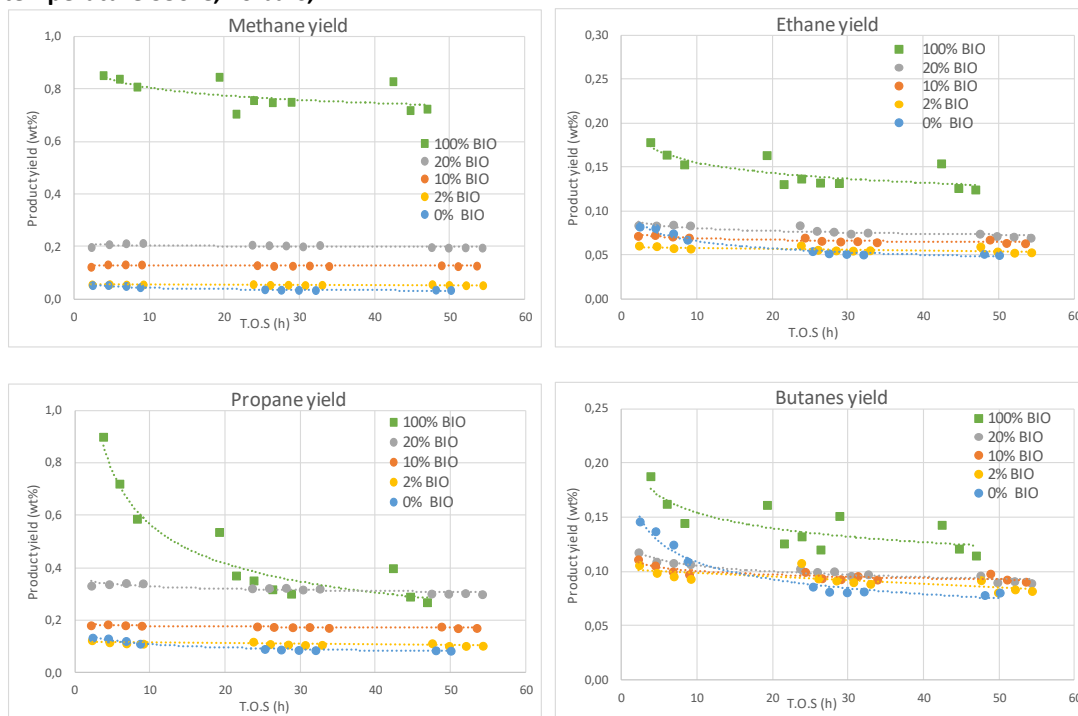
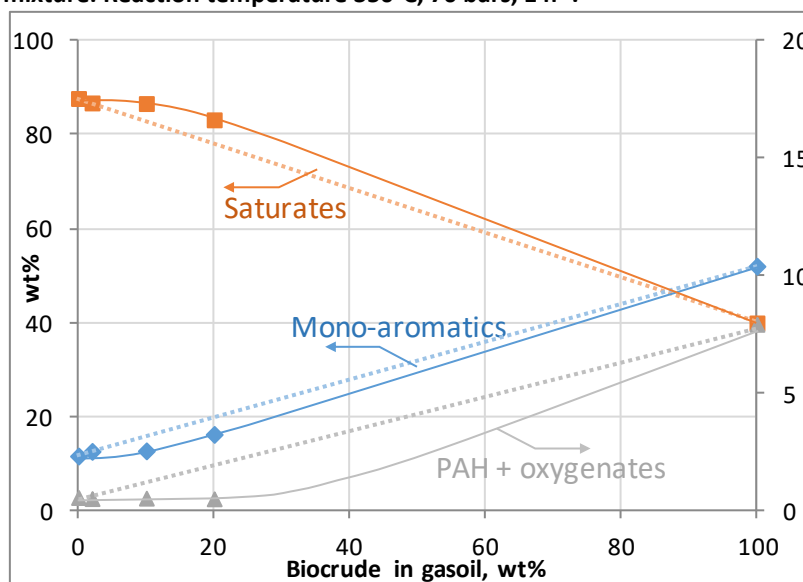


Figure 2. Hydroprocessed oil composition depending on the content of biocrude in the feeding mixture. Reaction temperature 350°C, 70 bars, 1 h⁻¹.



3.2. Comparison with Light Cycle Oil processing

Mixtures of 80% base stock with 20 % LCO or a blend of 10 % LCO and Biocrude were also processed as comparison to common refinery operation. The results relevant to this comparison are summarized in Table 2, runs 4, 6 and 7.

Upon replacing biocrude by LCO, the gas yield decreased linearly and went back to the same value than observed for the base stock. While ethane and butanes yields were similar for all mixtures, methane and propane yields increased linearly with the content of biocrude (Figure 3) as reported in the previous section. Water yield also decreased proportionally to the biocrude content. The boiling point distribution showed only minor differences, while the density of the hydroprocessed oil increased slightly with the amount of LCO in the mixture. This is reflected in the composition in the oil, with a slight decrease of saturates and a corresponding increase in the mono-aromatics content. The effect was found to be linear with the increasing amount of LCO and decreasing amount of biocrude in the feed mixture, as depicted in Figure 4. Also, a slight increase in polynuclear aromatics is observed, while the amount of oxygenated components remained very low within all the feed mixtures. These changes are consistent with the nature of LCO feed, which is very rich in polyaromatic structures.

None of the mixtures up to 20 wt% of LCO or Biocrude seems to experience deactivation during the 50 h on-stream of the testing, which was also reflected in the elemental analysis of the spent catalyst (Table 3). Only slight increase of the carbon content compared to the base case was observed for all the feed mixtures. By the contrary, the operation with 100% Biocrude showed a much higher coke-on-catalyst, which **may lead to premature catalyst deactivation in commercial operation. While possible with a standard hydrodesulphurization catalyst, it may be advantageous to carry the hydrodeoxygenation of unblended biocrude with an optimized catalyst in a separate operation, as it is done for example in the hydrotreatment of vegetable oils.**¹⁸

Table 3. Elemental Analysis of the spent catalyst recovered after 50 h on stream.

Feed / Element	C	H	N	S
100 % SRGO	1.9	1.5	0.2	9.0
+10% Biocrude	1.7	1.1	0.2	8.8
+20% Biocrude	2.2	1.7	0.1	8.0
+20% LCO	2.3	1.0	0.2	8.7
100% Biocrude	7.7	1.3	0.2	7.8

Figure 3. Detailed gas composition for several Biocrude and Light Cycle Oil contents in a blend containing 80 wt% SRGO. Reaction temperature 350°C, 70 bars, 1 h⁻¹.

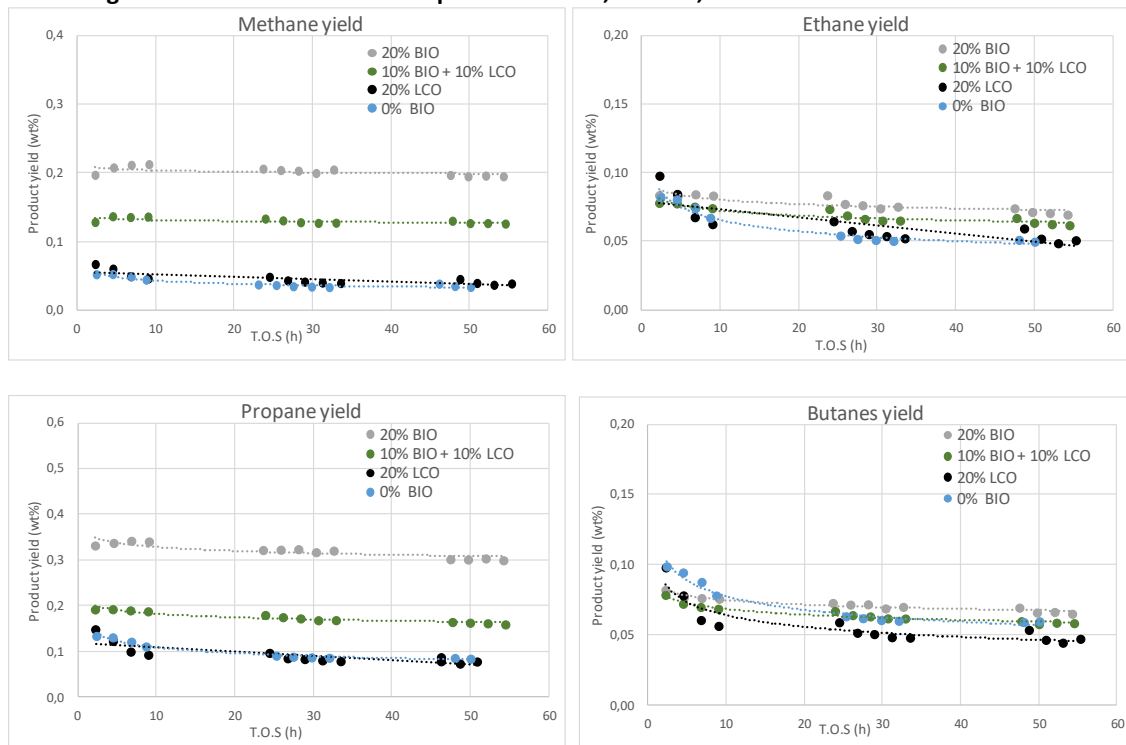
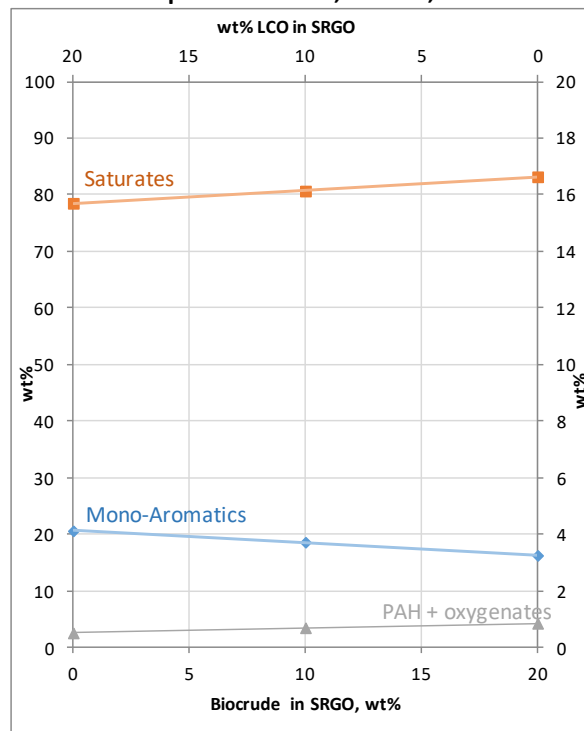


Figure 4. Hydroprocessed oil composition for several Biocrude and Light Cycle Oil contents in a blend containing 80 wt% SRGO. Reaction temperature 350°C, 70 bars, 1 h⁻¹.



3.3. GCxGC analyses of the hydroprocessed oils

Four hydroprocessed oils from SRGO, SRGO + Biocrude, SRGO + LCO and biocrude feeds are compared in Figure 5. Hydroprocessed SRGO gives an oil that is rich in n-paraffins, isoparaffins and naphthenes (highlighted area 1). Also, a number of compounds having two saturated rings can be observed (decahydronaphthalene core, area 2). Mono-alkyl aromatics families can be clearly seen in area 3, and are partially mixed with hydro-aromatics having one aromatic ring and one saturated ring (tetrahydronaphthalene core, area 4). A few diaromatics with a naphthalene core are observed in area 5. Meanwhile, the hydroprocessed biocrude showed much less paraffins and more saturated two-ring structures in the saturates fraction. Characteristic diterpene structures are also observed in the biocrude-derived oil, i.e. isomers of 18-norabietane ($C_{19}H_{34}$, area 6). These components may be derived from abietic acid ($C_{20}H_{30}O_2$), a main component of pine resin. A number of ring opening products ($C_{19}H_{36}$) are also observed. A large number of partially hydrogenated aromatic structures similar to diterpenes but with one aromatic ring ($C_{19}H_{28}$, area 7) are also characteristic of this hydroprocessed oil, as well as a number of hydro-aromatics with 14 to 16 carbons that are observed in area 4 and which may correspond to dealkylated products. This offers a good explanation for the surge of propane when processing biocrude, as the propyl group in norabietane-like structures would be easily cleaved. Some methyl fragment may be lost, contributing to increase methane yield. At the same carbon number, ring structures are significantly denser than alkane structures, as summarized in Table 4 for 14 carbon structures. As a result, in spite of similar distribution between families and a lower boiling point range, the density of the hydroprocessed oil may still increase when biocrude is incorporated into the base stock to be treated. Finally, the more polar, oxygenated compounds (area 8) are found below the PNA area. Mainly substituted methoxybenzenes and phenols, guaiacols, syringols and polyphenols were observed in this fraction. Notably, no acid, ketones or furans could be observed.

Table 4. standard density of several 14 carbon hydrocarbons

Compound	Formula	density (g/cm^3)
n-tetradecane	$C_{14}H_{30}$	0.764
Tetradecahydrophenanthrene	$C_{14}H_{24}$	0.914
Octahydrophenanthrene	$C_{14}H_{18}$	1.025
Tetrahydrophenanthrene	$C_{14}H_{14}$	1.060
Phenanthrene	$C_{14}H_{10}$	1.180

The biocrude/SRGO mixture resulted in a product composition similar to that obtained from just SRGO. However, the presence of characteristic diterpene components from the biocrude is clearly visible (area 9). An increase in hydro-aromatic structures is also observed compared to the base case. Moreover, various three-ring, saturated components (area 10) with 14 to 16 carbons ($C_{14}H_{24}$, $C_{15}H_{26}$, $C_{16}H_{28}$) are found, corresponding to dealkylated diterpenes. Qualitatively, the larger amount of fully hydrogenated diterpene structures, the lower amount of hydro-aromatics and the lack of oxygenated compounds indicate that the biocrude fraction in the mixture with SRGO experienced a more complete saturation and deoxygenation as compared to the case when the biocrude was treated alone. The lower space velocity associated with the biocrude (as it constitutes only 20% of the feedstock) and the lower catalyst

deactivation might best explain the greater biocrude upgrading depth of the biocrude in the biocrude/SRGO mixture.

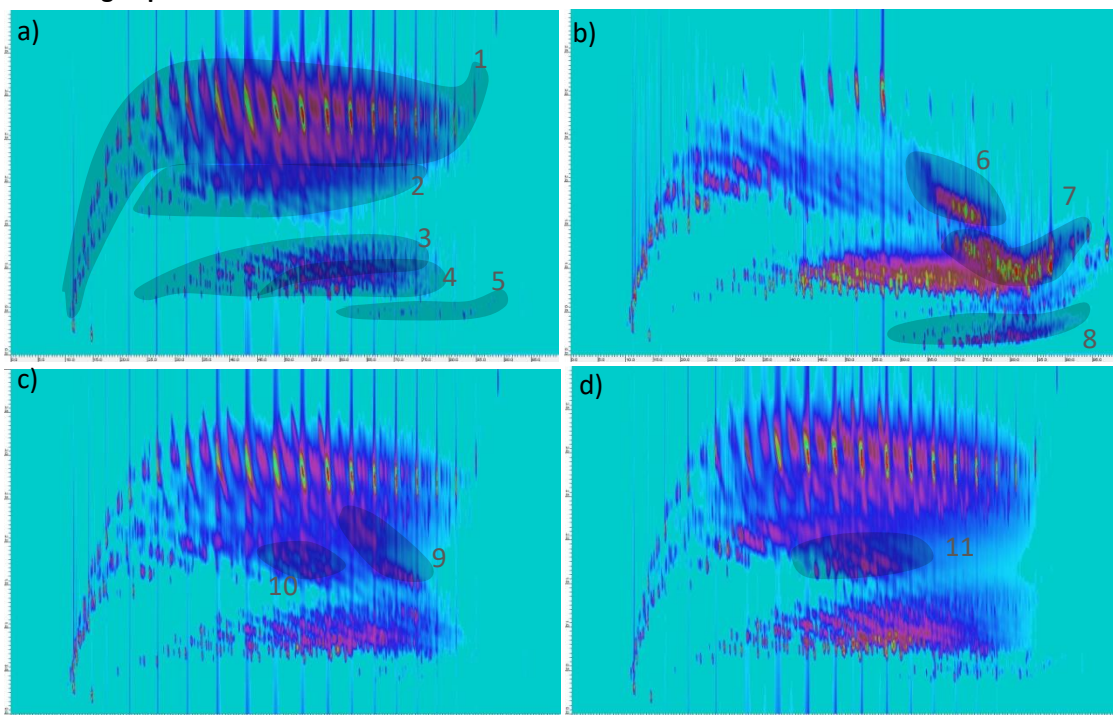
Finally, the oil from the SRGO-LCO mixture showed a characteristic increase of saturated three-ring structures of 12-16 carbons (area 11). LCO is very rich in di- and tri-aromatics of the naphthalene and phenanthrene/anthracene families, which have between 10 and 16 carbons. After hydrotreatment, the whole range of saturated and partially saturated compounds that could be derived from these aromatics is observed. As a result, the oils from the SRGO-LCO and SRGO-biocrude mixture had similar properties, with a slight advantage for biocrude-containing mixtures as they contained a slightly higher proportion of saturated structures.

The relationship between the groups listed in Table 2 and the areas indicated in the GCxGC data (see Figure 5 below) is as follows:

- Saturates includes areas 1, 2, 6, 9, 10 and 11
- Monoaromatics includes areas 3, 4 and 7
- Polynuclear Aromatics corresponds to area 5
- Oxygenated products correspond to area 8.

Figure 5. GCxGC chromatogram of hydroprocessed oils from: a) SRGO, b) Biocrude, c) 80/20 SRGO / Biocrude, d) 80/20 SRGO / LCO.

1: Paraffins, iso-paraffins and naphthenes. 2: Two rings naphthenes (decalin). 3: Monoaromatic with alkyl substituents. 4: Hydro-aromatics with one aromatic ring and one saturated ring (Tetrahydronaphthalene core). 5: Two and three aromatic rings. 6, 9: Three rings saturates (diterpenes). 7: Three ring hydroaromatics (1 aromatic and two saturated rings. 8: Oxygenated compounds. 10, 11: Three ring naphthenes



4. Conclusion

We have shown that up to 20 wt% of a biocrude obtained through catalytic hydrothermal treatment of biomass could be co-processed with a Straight Run Gasoil, yielding a hydroprocessed oil the boiling point range and density fully of which fully remain within diesel road specifications (EN590) and which has a very low content of oxygen. While mixtures with a high biocrude content might lead to premature catalyst deactivation **due to a higher coke formation** rate, keeping to lower amounts of biocrude provided a stable operation with complete hydrogenation of the oxygenates present in the feed during a 50 hours run **without a significant increase in coke on catalyst**. Compared to light Cycle Oil, a highly aromatic diesel range feed derived from catalytic cracking, the Biocrude was found to be easier to treat. A number of partially or fully hydrogenated structures with fused two- and three-rings explains the increase in density when processing biocrude, in a similar way to what is observed when processing blends containing LCO. A number of structures related to abietane are also observed, which are very likely to be derived directly from pine resin components. **In spite of the increase of mono-aromatics, the hydroprocessed diesel stream remains well inside specifications for blends of biocrude up to 20 wt%, with barely ant effect on PNA content.**

5. Acknowledgements

The authors thank Licella for providing the Biocrude and financial support. Licella gratefully acknowledges support from the Australian Government in the form of funding as part of the Advanced Biofuels Investment Readiness Program, received through the Australian Renewable Energy Agency (ARENA). Financial support by the Spanish Government-MINECO through program “Severo Ochoa” (SEV 2016-0683), CTQ2015-70126-R (MINECO/FEDER), and by the Generalitat Valenciana through the Prometeo program (PROMETEOII/2013/011) is also acknowledged.

6. Bibliography

- 1 BP Energy Outlook, 2017
- 2 U.S. Department of Energy. 2016. 2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy, Volume 1: Economic Availability of Feedstocks. M. H. Langholtz, B. J. Stokes, and L. M. Eaton (Leads), ORNL/TM-2016/160. Oak Ridge National Laboratory, Oak Ridge, TN. 448p
- 3 D. Klein-Marcuschamer and H.W. Blanch, *AIChE J.*, 61 (2015) 2689-2701
- 4 a) A. Corma, O. de la Torre and M. Renz, *Energy Environ. Sci.*, 5 (2012) 6328-6344; b) A. Corma, O. de la Torre and M. Renz, *ChemSusChem* 4 (2011) 1574-1577
- 5 P.M. Maitlis and A. de Klerk, *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*, ed. Wiley, 2013, chapter 16
- 6 F.M. Mercader, M.J. Groeneveld, S.R.A. Kersten, C. Geantet, G. Toussaint, N.W.J. Way, C.J. Schaverien, K.J.A. Hogendoorn, *Energy & Environmental Science* 4 (2011) 985-997
- 7 A.A. Lappas, K.G. Kalogiannis, E.F. Iliopoulou, K.S. Triantafyllidis and S.D. Stefanidis, *Wiley Interdiscip. Rev.: Energy Environ.*, 1 (2012) 285–297
- 8 R.H. Venderbosch, *ChemSusChem*, 8 (2015) 1306–1316
- 9 a) F. Goudriaan, D.G.R. Peferoen, *Chem. Eng. Sci.*, 45 (1990) 2729-2734, b) A.A. Peterson, F. Vogel, R.P. Lachance, M. Fröling, M.J. Antal and J.W. Tester, *Energy Environ. Sci.*, 1 (2008) 32–65; c) Y. Mathieu, L. Sauvanaud, L. Humphreys, W. Rowlands, T. Maschmeyer and A. Corma, *ChemCatChem*, 2017, DOI: 10.1002/cctc.201601677
- 10 S.A. Toor, L. Rosenthal and A. Rudolf, *Energy*, 36 (2011) 2328-2342
- 11 A. Oasmaa and S. Czernik, *Energy Fuels*, 13 (1999) 914–921
- 12 E.G. Baker and D.C. Elliott, *ACS Symposium Series*, 376 (1988) 228-240
- 13 D.C. Elliott and E.G. Baker, *Biotechnology and Bioengineering Symposium* (1984), 14(Symp. Biotechnol. Fuels Chem., 6th), 159-74
- 14 L.J. Humphreys, WO Pat. 2011/032020(A1), 2011
- 15 T. Maschmeyer, L.J. Humphreys, WO Pat. 2011/123897(A1), 2011
- 16 E. Furimsky, *Catalysts for Upgrading Heavy Petroleum Feeds*, *Stud. Surf. Sci. Catal.*, 169, 2007
- 17 H.P. Ruyter and J.H.J. Annee, *US Pat.* n° 4,670,613 (1987)
- 18 T. Kalnes, T. Marker, D.R. Shonnard, K.P. Koers, *Biofuels Technol.*, 4 (2008) 7-11