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Biofuels through Electrochemical transformation of intermediate BIO-liquids

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Deliverable 4.6 Report on the validation of biofuel blended with fossil-based fuel

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Description of the deliverable content and purpose

This EBIO public report covers the summary of validation of utilization of pyrolysis liquids in refineries to produce co-processed biofuels. Advantages of possible integrations, limitations and methodology pursued in EBIO for co-processing have been described. The report highlights the integration processes of bio-oils with conventional feedstocks in fluid catalytic cracking (FCC) units and hydro-processing units to produce co-processed biofuels. Additionally, the report addresses the technical requirements for making pyrolysis liquids "refinery-friendly” to ensure compatibility with existing refinery infrastructure.

Content

1. Introduction

The integration of upgraded pyrolysis liquids into refinery processes with minimal modifications presents a viable solution for decarbonizing the transport sector, particularly the aviation industry, which is one of the most challenging sectors to address. Utilizing existing infrastructure reduces the need for significant capital investments by making use of current FCC, hydro-processing and hydrotreating units. Allocating various advanced feedstocks to different hydro-processing units based on their properties and design limitations provides flexibility for incorporating renewables and producing targeted type of biofuel if the biocrude impurities (oxygenates, water and solids) are reduced and supported by catalyst modifications.

Pyrolysis liquids, also known as bio-oils, can be utilized in refineries through various processes to produce valuable fuels and chemicals. Here are some key points on how they are integrated into refinery operations:

- Pyrolysis liquids can be co-processed with conventional feedstocks in fluid catalytic cracking (FCC) units with vacuum gas oils. This integration allows for the production of mainly gasoline with lower carbon footprints.[1] Pilot tests of pyrolysis liquids treated over Ni-based catalysts can be co-processed in FCC units without technical problems, at substitution ratios of around 10 wt%. Co-processing treated liquids shows similar or slightly higher gasoline yields compared to pure VGO and no significant change in light cycle gas oil and heavies. [2]
- As depicted in Figure 1, hydro-processing involves a series of unit operations in refineries dedicated to different fuel types, such as naphtha, kerosene, diesel, and heavy fuels. In hydrotreating, heteroatoms like sulfur, nitrogen, and oxygen are removed without significantly changing the boiling point distribution. In hydrocracking, hydrotreatment is combined with hydrocracking to ensure C-C bond cleavage, resulting in lower boiling point ranges. Upgraded pyrolysis liquids can be processed in diesel hydrotreating or VGO hydrotreating and hydrocracking units, which typically operate under more severe conditions.
- In hydro-processing, a fixed bed operation is typically employed, necessitating an extended catalyst lifetime along with the use of high-pressure hydrogen, which is also consumed in the process. Given the chemical requirements and the properties of the resulting biofuel products, hydrotreating and hydrocracking can be utilized to co-process bio-oils and bio-crudes. This approach facilitates the incorporation of biofuel and biogenic carbon into the final products.

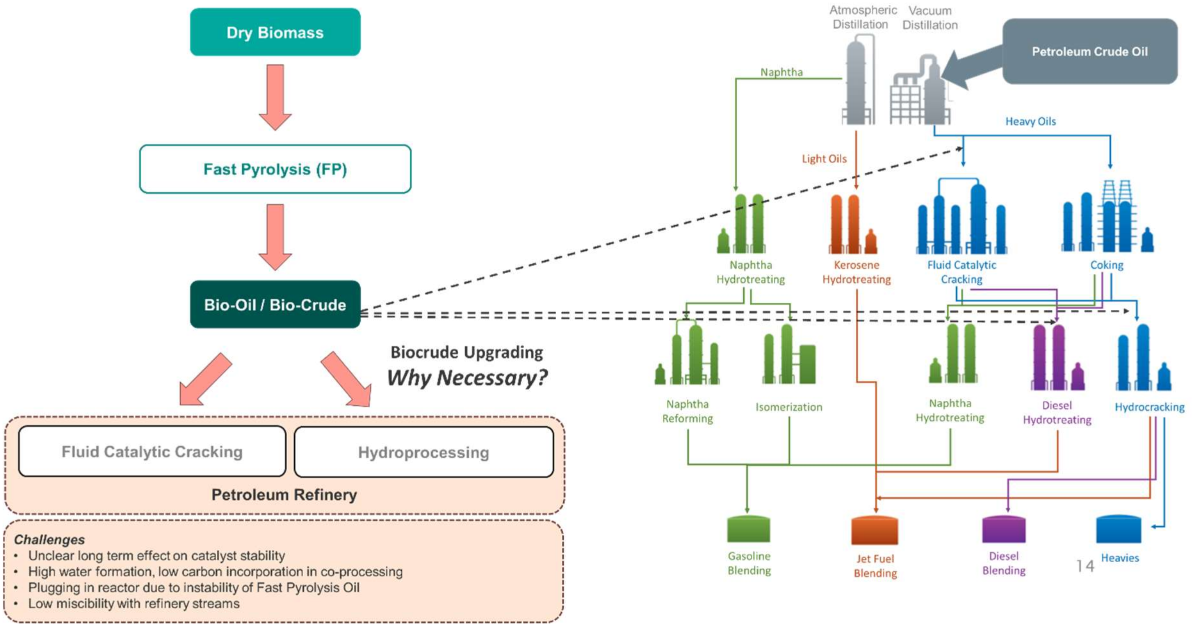
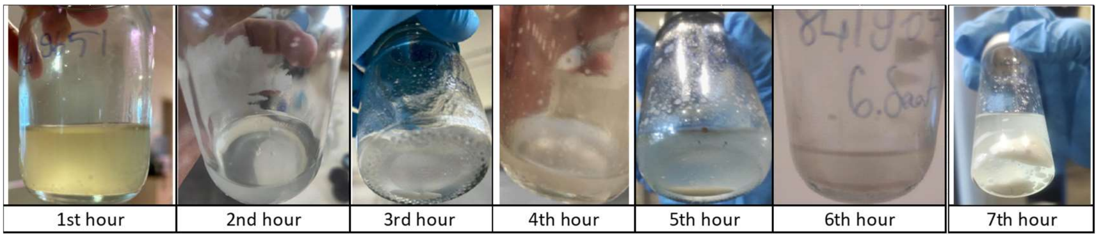


Figure 1. Possible pathways for utilization of pyrolysis oil in refinery processes

2. Methodology and Results

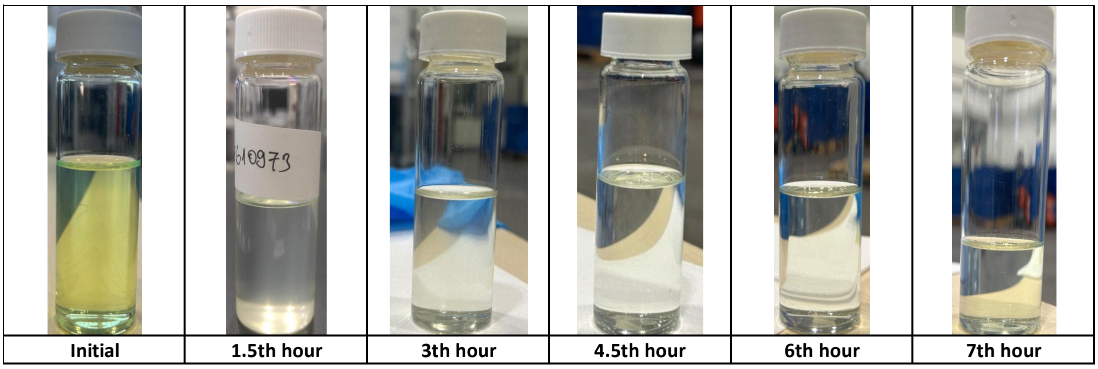
Although pyrolysis biocrudes are referred to as "crude," they differ significantly from petroleum crude in terms of molecular components, oxygen content, polarity, and acidity. Therefore, before co-processing in refineries, they should be upgraded either electrochemically or catalytically to produce bioliquids that are compatible with refinery streams. Otherwise, the rapid and irreversible catalyst deactivation in commercial units negates all the aforementioned economic advantages of co-processing.

In EBIO project, initial experiments involved the direct hydrotreatment of Stabilized Deoxygenated Pyrolysis Oil (SDPO) supplied by BTG. The effects of preheating, the addition of DMDS to SDPO, and various operational conditions were thoroughly investigated. Preheating to 220 °˚C prior to reaching the main reaction temperatures of 360-380 ˚°C was found to reduce polymerization and precipitate formation, so favors the formation of liquid products which are more stable, transparent and colorless. Similarly, hydrotreating of SDPO after removing the heavy fractions improves the appearance of hydrotreated products (Figure 3) compared to feeding whole SDPO at the same operational conditions (Figure 2). In all cases of standalone hydro-processing of SDPO, despite rapid hydrodeoxygenation and density reduction, tests revealed catalyst deactivation after a few hours. These findings suggest the potential benefits of leveraging the dilution effect of co-processing and fractionation for smoother integration into refinery hydro-processing operations.



1st hour | 2nd hour | 3rd hour | 4th hour | 5th hour | 6th hour | 7th hour

Figure 2. Total liquid products obtained after standalone hydroprocessing of SDPO without fractionation



Initial | **1.5th hour** | **3th hour** | **4.5th hour** | **6th hour** | **7th hour**

Figure 3. Total liquid products obtained after standalone hydroprocessing of fractionated lighter SDPO (boiling point < 450 ˚C)

Atmospheric and vacuum distillations are essential operations for processing crudes with a large boiling point distribution, such as SDPO (T5-T95 (wt%) ~70-595 °C) When followed by the subsequent upgrading processes distillation steps help maximize the production of valuable products, such as kerosene, and prevent the unnecessary use of the hydroprocessing unit's volume capacity on fractions that are not within its design scope. Therefore, considering the instable nature of the SDPO fractionation under controlled vacuum offers significant benefits in co-processing by providing two primary technical advantages:

- Adjusting the boiling point range and solubility of biofeed in related fossil streams such as kerosene, diesel, and light cycle gas oil,
- Eliminating heavy components in biocrude causing the blocking of active sites of the catalysts and deactivation.

In co-processing, the initial step involves identifying a primary fossil feed in which SDPO is fully soluble. While SDPO does not dissolve well in straight run diesel due to polarity mismatch, light cycle gas oil (LCGO), which is a highly aromatic heavy product of FCC, is capable of dissolving 5 vol.% of SDPO. According to turbiscan analysis, the stability of the mixture deteriorates when the concentration of biofeed increases to 10 vol.% and 20 vol.%. Therefore, all co-processing trials were performed with the concentration set at 5 vol.%.

In lab and long-run pilot scale co-processing tests of 5 vol.% SDPO + LCGO over NiMo/Al_2O_3 catalyst, heteroatom removal, C-C bond cleavage, hydrogenation, and aromatic saturation were monitored by simulated distillation, elemental analysis, polyaromatic hydrocarbon analysis, density, and chromatographic techniques such as fluorescent indicator absorption and reformulyzer throughout the continuous reaction via hourly samples (Figure 4).

Upon screening the effect of LHSV, pressure, and temperature, a 180+ hours run at optimized conditions revealed efficient reduction of aromatic content from 73 wt.% (23 wt% monoaromatics and 50 wt.% diaromatics) to total aromatics of 18 wt.%, with the majority being monoaromatics (17 wt.%). This indicates an efficient conversion of aromatic molecules to naphthenics, which were detected to be present in 72 vol.% in the kerosene cut of the hydrotreated product after fractionation.

Initially, the sulfur content of 26000-27000 ppmw and nitrogen content of 520-600 ppmw in the feed blend were reduced to 150 ppm and 0.03 ppm, respectively, in the total liquid product. The initial density of the 5 vol.% SDPO + LCGO at 955 kg/m^3 proceeded within the 840-848 kg/m^3 interval for 180+ hours time on stream, with a hydrogen content of 13-14 wt%. According to SIMDIS data, the product distribution into naphtha (bp <150 ˚C), kerosene (bp 150-300 ˚C), and diesel (bp 300-370 ˚C) cuts was in the range of 4-5 wt.%, 80-87 wt.%, and 8-12 wt.%, respectively.

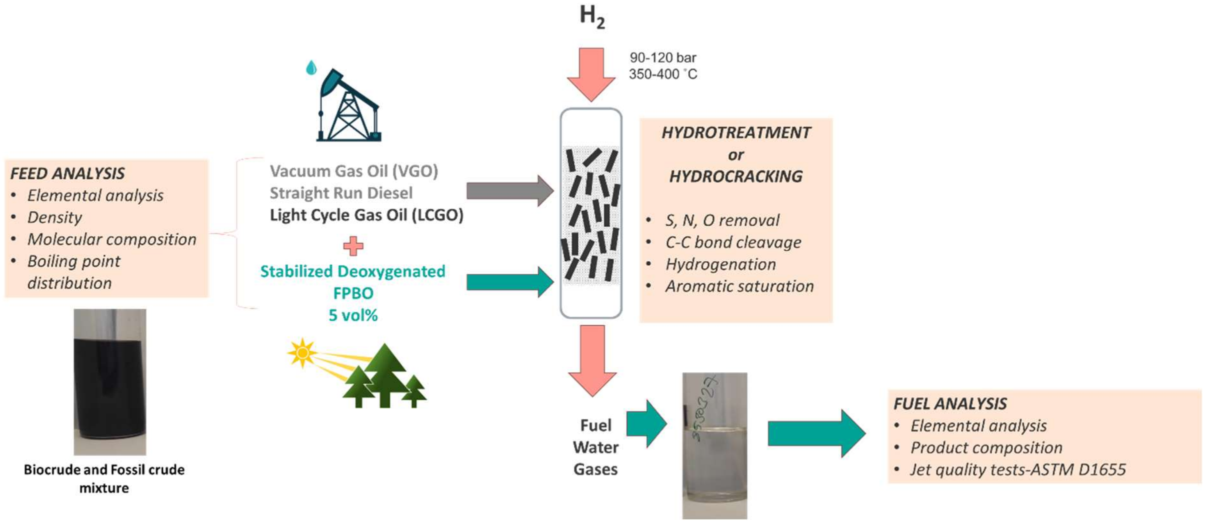


Figure 4. General approach in co-processing

The quality of the kerosene fraction was evaluated against the ASTM D1655 Jet A-1 specifications. The analysis confirmed that the aromatic content, flash point, freezing point, olefin content, D86 distillation temperatures, and water content met the required standards. Future studies will include ^{14}C AMS analysis to precisely determine the retention of biogenic carbon within the jet fuel.

3. Conclusion

The validation of biofuel blended with fossil-based fuel, as detailed in this report, demonstrates significant advancements in the integration of pyrolysis liquids into refinery processes. The findings highlight the potential of co-processing stabilized pyrolysis oil with conventional feedstocks in hydro-processing units, resulting in the production of valuable fuels with lower carbon footprints.
Key findings include,

- **Standalone Hydro-processing**: Initial experiments with Stabilized Deoxygenated Pyrolysis Oil (SDPO) showed that preheating and fractionation enhanced the stability and appearance of hydrotreated products. Nonetheless, the rapid catalyst deactivation observed with neat SDPO indicated that it would be more reasonable to benefit from the advantages of vacuum distillation and process the lighter fraction of SDPO to preserve the catalyst stability in long term. However, this also needs further investigation in terms of cut point temperature of SDPO distillation and hydrotreatment reaction run time.

- **Co-processing**: Coprocessing trials with Light Cycle Gas Oil (LCGO) and SDPO (5 vol%) over NiMo/Al_2O_3 catalyst showed efficient reduction of aromatic content and significant sulfur, nitrogen and oxygen removal. Also, an effective transformation of aromatic compounds into naphthenic structures, thereby enhancing the production of jet fuel convenient with the standard specification.

The results from the EBIO project provide a promising pathway for the sustainable co-production of biofuels in refineries with existing infrastructure, contributing to the broader goals of reducing greenhouse gas emissions in aviation sector.

4. References

[1] Lutz, H.; Büchele, M.; Knaus, F.; Reichhold, A.; Vollenhofer, W.; Venderbosch, R. Wood Derived Fast Pyrolysis Bio-liquids as Co-feed in a Fluid Catalytic Cracking Pilot Plant: Effect of Hydrotreatment on Process Performance and Gasoline Quality. *Energy Fuels* **2022**, *36*, 10243-10250

[2] Wang, C.; Venderbosch, R.; Fang, Y. Co-processing of Crude and Hydrotreated Pyrolysis Liquids and VGO in a Pilot Scale FCC Riser Setup. *Fuel Process. Technol.* **2018**, *181*, 157-165.