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Production of Hybrid Fuel from Fossil- and Bio-based Intermediates Hydrotreatment Assessment Using Aspen Model: Energy and Environmental Profile

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In recent years, the increasing demand of diesel fuel has led the scientific community and the industry to investigate new technologies and feedstocks for diesel production. Light Cycle Oil (LCO) could be an interesting substitute for diesel fuel as it presents a similar boiling range to diesel. LCO upgrading can be achieved via catalytic hydroprocessing, a refinery-based technology, enabling heteroatom (sulfur, nitrogen, metals) removal and saturation of olefins and aromatics. LCO hydrotreatment took place in the hydroprocessing unit at the Chemical Process & Energy Resources Institute of the Centre for Research and Technology Hellas and was used as a base case, and then the co-hydroprocessing of LCO with Waste Cooking Oil (WCO) was investigated as a means to improve the properties of LCO while improving the end fuel carbon foot-print. The results showed that there are some inhibitory properties like heavy sulfur species, which are difficult to be removed via hydroprocessing. For this reason, the fractionation of LCO up to 350 °C was performed with the objective of isolating these heavy sulfur species and some other polyaromatic compounds that are difficult to be removed. The light fraction of LCO (LCO_cut) was led for hydroprocessing and then was also mixed with WCO and co-hydroprocessed. In this study, all these four experimental hydroprocessing cases are developed in an Aspen simulation model of a hydrotreating process using experimental process data in order to evaluate how the distillation and the WCO addition affect the LCO hydrotreatment process. The results have shown that the combination of LCO distillation and WCO addition renders high quality compatible hybrid products, presenting the most favourable environmental profile, as compared to the other examined cases. In particular, the case of co-hydroprocessing of LCO_cut with WCO addition presents the lowest environmental impacts, leading to a reduction of about 2-12 % of GHG emissions, rendering this pathway more sustainable and attractive for the refinery industry.

1. Introduction

Light Cycle Oil constitutes one of the most challenging refinery streams that can be potentially valorised, attracting more and more the interest of the scientific community (Anilkumar et al.,2020). LCO is one of the main products from the fluid catalytic cracking (FCC) unit, the yield of which varies between 20 and 50 %. Nevertheless, the high percentage of sulfur and aromatic compounds as well as the low cetane number of LCO make its upgrading difficult enough (Palos et al., 2018). Until now, several studies from industrial and academic sectors have made efforts to improve LCO quality and meet the current stringent diesel fuel specifications via hydroprocessing, a widespread technology applied in refineries for upgrading fossil fuels ranging from light petroleum naphtha to vacuum gas oils (VGOs) and residues. According to the author’s previous research, the hydroprocessing of the pure LCO and the co-hydroprocessing of LCO with WCO were investigated. The results showed that the presence of WCO improved the main properties of the final hydrotreated (HDT) product like density, cetane number and polyaromatic hydrocarbon but the sulfur content remained high due to the heavy sulfur species met in LCO. For this reason, a distillation of LCO up to 350 °C was performed with the objective of isolating the heavy sulfur species which are difficult to be removed via hydroprocessing. The light cut of the LCO distillation, LCO_cut, which had an improved content of inhibitory compounds, was used as a feed in a

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hydroprocessing unit in order to get a final product that could approach diesel quality. So, in the second stage of the previous study, the hydroprocessing of LCO_cut and the co-hydroprocessing of LCO_cut with WCO were investigated (Dagonikou et al., 2021). Until now, all these four cases were evaluated from the point of view of evaluating the final product quality. The results showed that the distillation contributed positively to the co-hydroprocessing of LCO with WCO with the intention of LCO upgrading as most of the properties meet or are not too far from the EN590 diesel specification.

The scope of this study is to go one step further by evaluating the environmental profile of these four case studies through simulation via an LCA study. LCA is a standardized methodology frequently applied to biofuels systems, while limited studies have evaluated the environmental performance of bio-based and fossil-based intermediates towards hybrid fuels. Therefore, there is a lack of detailed inventory data for these studies (Petrescu et al., 2021), and these assessments have to be based primarily on process simulation.

The hydroprocessing of LCO and LCO_cut (pure or with WCO) was developed using Aspen Plus simulation and the results occurred, and were used for the environmental assessment.

2. Methodology

This section involves a detailed description of the aforementioned four experimental hydroprocessing cases developed in an Aspen simulation model. The model was based on real process data from the authors' previous work (Dagonikou et al., 2021) simulating the hydroprocessing of four different feedstocks; LCO, LCO_cut, LCO/WCO and LCO_cut/WCO. All these experimental data were obtained from the hydrotreatment of these four feedstocks taking place in the hydroprocessing unit at the Chemical Process & Energy Resources Institute (CPERI) of the Centre for Research and Technology Hellas (CERTH). Initially, the LCO hydrotreatment was used as a base case and then the co-hydroprocessing of LCO with WCO was investigated as a means to improve the properties of LCO while improving the end fuel carbon footprint (Dagonikou et al., 2021). The results exported showed that hydroprocessing is not an adequate technology for LCO upgrading, pure or with WCO, in order for the final HDT product to be used as one of the blending components of the diesel fuel pool. For this reason, a distillation of LCO up to 350 °C was performed with the objective of isolating the heavy sulfur species and polyaromatic compounds which are difficult to be removed via hydroprocessing. The light fraction of LCO (LCO_cut), free from heavy refractory compounds, was led for hydroprocessing pure and with WCO in a 90/10 (v/v) ratio. The experimental conditions and results were input into a process simulation model for determining the mass and energy flows at the scale of 48 t/h LCO production. The data of all these aforementioned hydrotreating experiments were simulated in an Aspen model in order for these technologies to be evaluated from an environmental viewpoint. The environmental evaluation of these case studies was realized using the LCA methodology. In particular, the present LCA study aims to attain the environmental characteristics of the four intermediates production processes based on the Aspen simulation results (Figure 1).

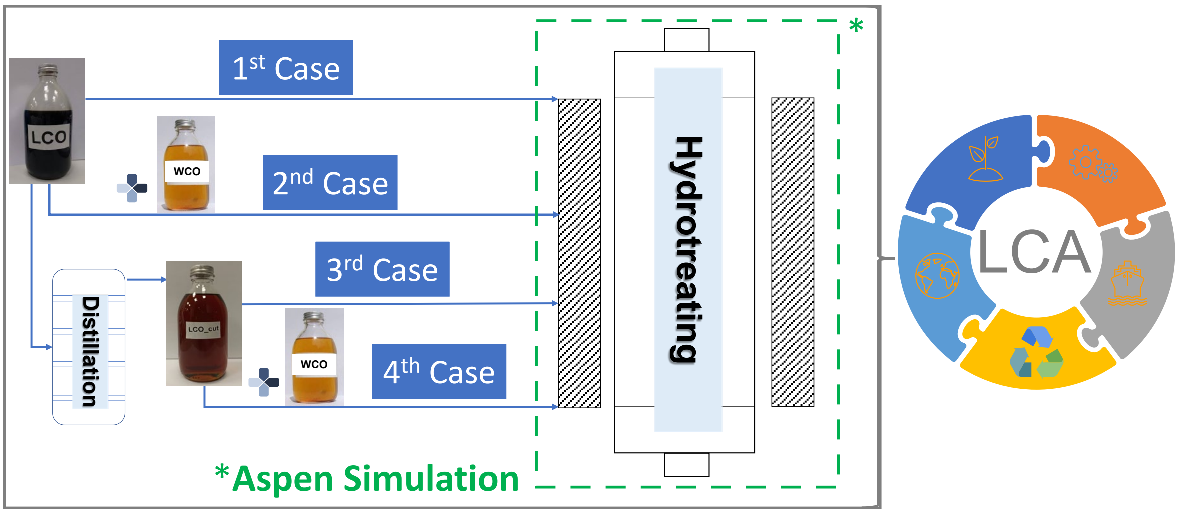

Figure 1: Methodology of the energy and environmental assessment of the four case studies

GEMIS (Global Emission Model for Integrated Systems, Version 4.9) was used to complete the inventory development, while data were also retrieved from literature.

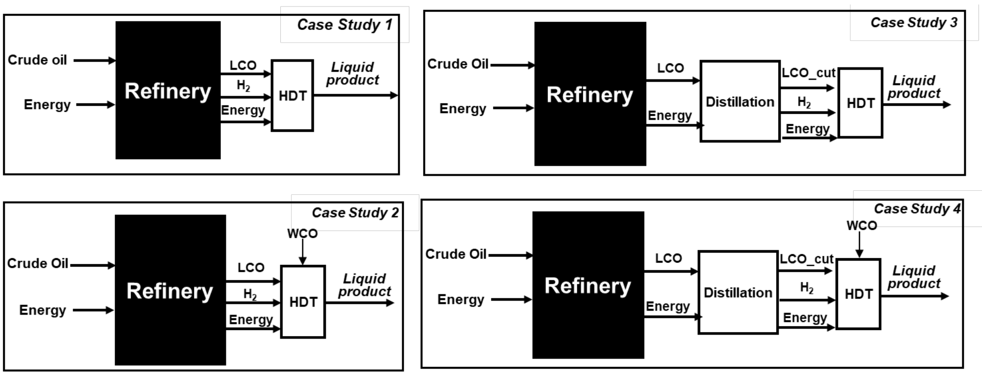

Figure 2: System boundaries of the four case studies of intermediates production processes applied in the LCA study

3. Process Simulation

For the purpose of scaling up the lab-scale hydrotreating process, a process simulation model was built to compute the mass and energy balances, based on the experimental conditions and results as shown in Figure 3. Aspen Plus is a process simulation software frequently employed to design and techno-economic analyses of different refinery processes (Cavalcanti et al., 2022). The Aspen Plus (Version 2011) was evaluated using the Peng-Robinson-Boston-Mathias (PR-BM) modelling approach for the base method as this method is suitable for petrochemical processes (Rosha et al., 2022).
In Section 4, an assumption was considered regarding the environmental performance of the distillation stage. According to the literature, the crude oil distillation process energy consumption corresponds to 20 % of the total refinery energy demands (Durrani et al., 2018). In the case that LCO is distilled in LCO_cut and heavy fraction, the electricity consumption of this distillation stage is assumed to be 5 % of the total refinery energy demands.

3.1 The development of process simulation

Regarding the flow rate, a European average refinery capacity of 960,000 kg/h was considered. Approximately 5 % of its capacity corresponds to LCO production. The LCO accounts for 15 % of FCC's total products and 5 % of the total refinery capacity as the FCC unit capacity varies between 20-50 % of total refinery capacity (Su et al., 2021). Assuming that 5 % of this capacity corresponds to the LCO hydroprocessing unit, a capacity of 48,000 kg/h was selected.
In the case of LCO_cut (pure or with WCO) hydroprocessing Aspen simulation, the inlet liquid feed was considered as 38,400 kg/h as a part of LCO remained in the heavy fraction via distillation. According to the real experimental data, the distillation yield corresponds to 80 % for LCO_cut and 20 % for the heavy LCO fraction. This data is adjusted to industrial-scale considering the input liquid flow of LCO to the distillation column of about 48,000 kg/h, as explained in the previous paragraph. The LCO_cut exited from the distillation column corresponds to 38,400 kg/h, while the heavy fraction corresponds to 9,600 kg/h.
In total, four cases were developed in Aspen Model; LCO hydroprocessing, LCO/WCO co-hydroprocessing, LCO_cut hydroprocessing and LCO_cut/WCO co-hydroprocessing. The data used for developing the hydrotreatment (HDT) diagram in Aspen, include and combine data from authors' prior experimental studies, literature data and some assumptions. The liquid feedstocks and products were characterized as a petroleum assay using the density and the distillation curve properties, as it is difficult to be determined due to its hydrocarbon composition complexity. The development of the reaction system was defined as a black box, considering the actual experimental data for the composition of liquid feeds and products, while the precise composition of all input and output streams was based on the authors' previous work.
The selected operation conditions in Aspen Model were typical HDT conditions applied in the refinery. Especially, the temperature was 360 °C, the pressure was 8.2 MPa, the Liquid Hourly Space Velocity (LHSV) was 1 h^{-1}, the H_2/oil ratio was 500 L of H_2/ L of liquid feed while a commercial NiMo/γ-Al_3O_2 catalyst was used in real HDT experiments.

3.2 Flow sheet description

The proposed process flowsheet (Figure 3) in this work was based on the works of Dagonikou et al. (2021). The liquid feed flow for the LCO hydroprocessing and for the LCO/WCO co-hydroprocessing corresponds to 48,000 kg/h based on the aforementioned assumptions, while for the case of the LCO_cut hydroprocessing and for the

LCO_cut/WCO co-hydroprocessing the feed flow is 38,500 kg/h as a part of the feedstock has remained as the heavy fraction via distillation.

The liquid stream (LIQ FEED) is pumped (PUMP), mixed (MIXER1) with the recycled hydrogen stream (RECYCLE1), and heated via heat exchangers (HX1, HX2, and HX3) and finally via furnace (FURNACE) to 360 °C. The mixture is led to the reactor system with the make-up H_2 which corresponds to the H_2 consumed for the HDT reactions. The product exiting from the reactor enters a separation system via a heat exchange sequence where the heat of the HDT product is exploited. The reaction products are flashed out together with the H_2 gas by a series of separators for achieving a separation between the liquid and gas products. The gas stream is depressurized in a turbine exploiting high pressure for electricity generation and then led to the LPLT (Low-Pressure Low Temperature) separator for H_2S removal from the gas stream. The other gas products such as methane, ethane, and propane, are removed via a mixer (MIXER4) to purge while the gas stream RECYCLE, including mostly H_2, is recycled to the unit. The final liquid product (23) is led to the distillation unit (DISTIL) in order for the heavy fractions to be removed from the middle distillate fractions (gasoline, jet and diesel fuel).

In the case of WCO addition in the feedstock, three extra by-products are produced; CO, CO_2 and H_2O. For this reason, two additional separators are added in order for the CO_x and the H_2O to be removed via SEP1 and SEP2. In the case of LCO and LCO_cut HDT process, these two separators do not exit as CO_X and H_2O are not produced due to O_2 absence in the feedstock.

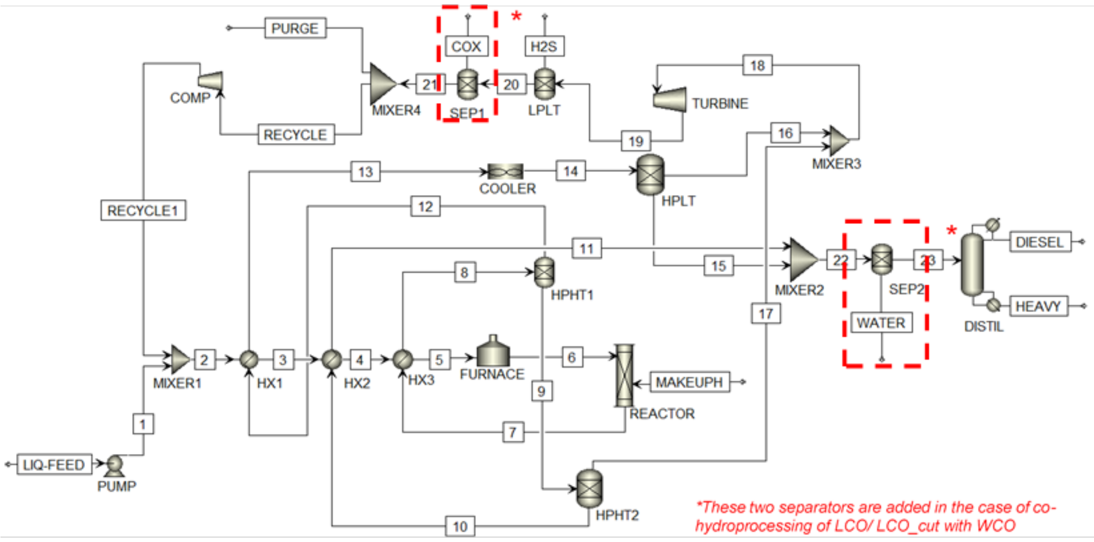

Figure 3: Flow diagram of the hydroprocessing simulation

3.3 Simulation results

After configuring all process inputs, the steady-state simulation was completed without convergence errors. In Table 1 the energy demands (including electricity and fuel gas) and the H_2 consumption of each case are depicted as well. An estimation of energy requirements for the LCO distillation is presented. The results depicted in Table 1 are based on the petroleum fraction yield as the heavy fraction is a low-quality product, not commercial, but it is used for heating requirements of a refinery. According to the results, the energy and make up H_2 consumption of the simulated HDT processes is depicted per m^3 of total liquid product. It is worth noting that as total liquid product is considered the middle fractions (naphtha, jet and diesel fuel) which are final market products.

Table 1: Energy and make up H_2 consumption (per m^3 of total liquid product) of the simulated HDT processes

	LCO HDT process	LCO/WCO HDT process	LCO_cut HDT process	LCO_cut/WCO HDT process
Pump (J/m^3)	1.29E+04	1.28E+04	1.29E+04	1.27E+04
Compressor (J/m^3)	1.31E+05	1.35E+05	1.32E+05	1.05E+04
Turbine (J/m^3)	3.95E+04	4.15E+04	4.16E+04	3.26E+04
Total Electricity (J/m^3)	1.04E+05	1.06E+05	1.03E+05	8.53E+04
Fuel Gas (J/m^3)	1.81E+08	1.79E+08	1.81E+08	1.61E+08
H_2 Consumption (kg H_2/m^3)	24.87	20.82	22.17	17.06

Another important parameter which is worthy to be evaluated is the yield of the final liquid products that can be commercially used such as naphtha, jet and diesel fuel. Considering distillation range of every final liquid product, a distribution of petroleum fractions was realized. The term "middle distillates" is assigned to petroleum commercial products obtained in the "middle" boiling range between 180 °C and 360 °C during the process of crude oil distillation. In Figure 4, the yield (% v/v) of the total liquid product for ever petroleum fraction is depicted for final HDT product of each case. As depicted in Figure 4, in the case of LCO_cut, pure or with WCO, the final HDT result is totally in the range of useful products, as it is expected due to the distillation of LCO which preceded.

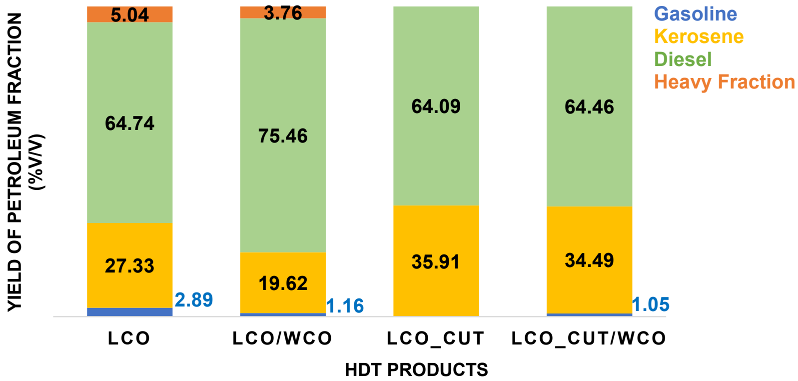

Figure 4: Petroleum fractions yield of HDT product

4. Environmental Performance

Global Warming Potential (GWP) is considered for the environmental assessment of the investigated case studies showing the contributions in terms of equivalent CO_2 emissions per functional unit taking into account (kg CO_2 eq/m^3 of total liquid product). The functional unit used in the study is 1 m^3 of the total liquid product.
The greenhouse gas (GHG) emissions results of the four examined case studies are presented in Table 2, and as it is observed the case study incorporating the LCO/WCO and LCO_cut/WCO production processes offer products with lower emissions, as compared with LCO and LCO_cut processes. These results validate that the exploitation of fossil-based and renewable-based feedstocks as intermediates toward hybrid fuels constitutes favourable environmental processes. Due to limited relevant LCA studies, the comparison of these results with other works is not feasible.
The refinery emissions associated with the production of LCO are the major source of the GHG emissions for all the four case studies as depicted in Table 2. The WCO incorporation in the liquid feed obviously seems to have a positive effect on GHG emissions both in the case of studies 2 and 3 in comparison with the corresponding ones of pure LCO and LCO_cut hydrotreatment. The hydrotreating units contribute significantly to the GHG emissions of the final products, due to H_2 consumption. The distillation stage incorporation of the liquid feed increases the GHG emissions in the 3rd case study, but in the 4th case study, the combination of distillation and of WCO addition renders the most environmentally friendly fossil- and biobased intermediates.

Table 2: GWP emissions of the examined case studies (kgCO$_2$-eq/m^3 of total liquid product)

Process stage	Case study 1	Case study 2	Case study 3	Case study 4
Refinery	33.855	30.589	34.104	29.962
HDT LCO	0.0565	-	-	-
HDT LCO/WCO	-	0.0537	-	-
HDT LCO_cut	-	-	0.0579	-
HDT LCO_cut/WCO	-	-	-	0.0464
Total	33.911	30.643	34.162	30.008

5. Conclusions

According to the results of the current study, the LCO_cut hydroprocessing not only contributes positively to the quality of the final liquid product, but it leads also to a high yield of commercial mid-distillates products. So, it is worth noting that although a part of LCO (about 20 %) was removed during the initial distillation, the final high-quality products by LCO_cut hydroprocessing and by LCO_cut/WCO co-hydroprocessing, can potentially be mixed in a higher percentage with the commercial fuels. Regarding the H_2 consumption, it is obvious that the fourth case of LCO/WCO co-hydrotreatment presents the lowest H_2 requirements per m^3 of the final hybrid liquid product. This observation is important as H_2 consumption is an important parameter for refineries in terms of economic viewpoint. Co-processing of fossil- and biobased intermediates were found to be an interesting option from an environmental perspective for the production of hybrid fuels in both cases (LCO/WCO and LCO_cut/WCO), in comparison to the processing of the individual stream (pure LCO and LCO_cut). Based on the LCA results the LCO_cut/WCO product presents a favourable environmental profile compared with all the other cases, presenting the lowest CO_2 emissions, about 30 kgCO_2-eq/m^3 of total liquid product. This study forms the basis for future research on optimizing the technologies of the LCO distillation and of the LCO/ WCO co-processing, rendering this pathway more attractive from an environmental viewpoint.

Nomenclature

CO – carbon monoxide
CO_2 – carbon dioxide
CO_x – Carbon monoxide and dioxide
GHG - Greenhouse gas
GWP – Global Warming Potential
HDT – hydrotreatment/hydrotreated
LCA – Life Cycle Assessment
LCO – Light Cycle Oil
LCO_cut – Light Cycle Oil_cut
WCO – Waste Cooking Oil

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