UPGRADED PYROLYSIS BIO-OIL AS ALTERNATIVE RENEWABLE SUPPLY IN CLASSICAL PETROLEUM REFINERY PROCESSES

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SUMMARY
The production of renewable liquid fuels for transport has attracted international research and market interest in line with the ambitious 2020 and 2030 energy and climate targets set by the European Union (EU) policy, considering the increasing global demand for their fossil counterparts and the resulting environmental impact. In this frame, the study investigates refinery-compatible entry points to directly co-feed bio-based refinery intermediates and further co-process them in existing petroleum crude oil refineries. The studied pyrolysis bio-oil has been produced via ablative fast pyrolysis and upgraded via mild hydrotreatment (HDT) in order to fulfill refineries' specifications and become a "drop-in" biofuel in compatible refinery "location". Five typical fossil-based refinery intermediates have been selected as potential candidates for co-processing. The miscibility of the aforementioned renewable and conventional fuels has been investigated. Among the refinery streams, Fluid Catalytic Cracking Light Cycle Oil (FCC LCO) has been identified as the most promising candidate for co-processing, resembling HDT-Bio-oil's properties.

INTRODUCTION
The current strategic framework for a Resilient Energy Europe, having set ambitious 2020 and 2030 energy and climate targets, calls for energy security, a decarbonized economy and a fully-integrated and competitive European energy market. Toward this direction the European Industrial Bioenergy Initiative, launched under the Strategic Energy Technology Plan, prioritized pyrolysis technology among the most promising ones [1]. Therefore, international research is being conducted on developing and further validating strategies and innovative technological pathways that will overcome techno-economic limitations associated with the valorisation of pyrolysis bio-oil, as an alternative and renewable transport fuel. In this respect, pyrolysis bio-oil refinery integration appears to be of great perspective.

The main premise of this study is to overcome the key technological challenges of co-processing refinery intermediates with the newly developed bio-based intermediates, i.e. hydrotreated pyrolysis bio-oils (BioMates). Toward this direction, phase bahavior and fuel properties of HDT-Bio-oil and refinery intermediates have been evaluated to: (a) indicate the physicochemical relativity between the liquids that will form the mixtures and (b) show the effect of HDT Bio-oil addition to the refinery stream, in the underlying process.

The study is part of the "BioMates" Horizon2020 research and innovation EU project, aspiring in combining innovative 2nd generation biomass conversion technologies for the cost-effective production of reliable bio-based intermediates that can be further upgraded in existing oil refineries as renewable and reliable co-feedstocks. Therefore, the current miscibility study acts as a pre-screening of candidate feedstocks for the targeted hydroprocessing study that will follow.

TARGETS AND METHODOLOGY
HDT-Bio-oil co-processing with refinery streams and validation that renders reliable late-stage research operation data, necessitated a miscibility study to identify compatibility of bio-based

feedstocks with refinery's intermediates. In this study, the following refinery streams have been selected as potential candidates for co-processing with HDT-Bio-oil:

- Straight Run Distillate Diesel (SRGO)
- Atmospheric Gasoil (GASOIL)
- Light cycle oil (FCC LCO)
- Heavy cycle oil (FCC HCO)
- Light vacuum gas oil (LVGO)

The homogeneity of the two types of feedstocks is initially assessed via a miscibility study, as a pre-screening step of the candidate refinery intermediate for the co-hydroprocessing study that will follow. In particular, the miscibility of the aforementioned renewable and conventional fuel intermediates has been investigated via light microscopy. The properties of HDT-Bio-oil and those of the most promising candidate for co-processing (i.e., boiling curve, gravity/density, overall elemental composition, viscosity, surface tension) were compared and evaluated. The quality properties of typical refinery streams serve as the basis to define HDT-Bio-oil specifications for refinery integration.

EXPERIMENTAL PART

Refinery intermediates and mild-hydrotreated 2nd generation biomass bio-oil samples were used for the purposes of the current miscibility study. Mild hydrotreated ablative pyrolysis oil (HDT-Bio-oil) was mixed to ~30 vol% with fossil-based refinery intermediates in order to evaluate the potential miscibility and moreover reactability leading to agglomerates that can prohibit catalytic hydroconversion. In particular, typical 2017 fossil-based refinery intermediates from a European BP refinery and upgraded bio-oil from University of Chemistry and Technology, Prague (UCTP) were delivered to Centre of Research and Technology, Hellas (CERTH), in order to study possible refinery entry points and specs for HDT-Bio-oil. The received HDT-Bio-oil and refinery intermediates were stored in a cool room (-6 °C) prior to experiments, to avoid degradation. Regarding bio-oil, the aqueous phase was separated prior to experimentation using a balloon separator.

The refinery streams that have been investigated as potential candidates for co-processing with HDT-Bio-oil are the following: Straight Run Distillate Diesel (SRGO); Atmospheric Gasoil (GASOIL); Light cycle oil (FCC LCO); Heavy cycle oil (FCC HCO); Light vacuum gas oil (LVGO). As part of the methodology, the different samples were microscopically "scanned" in order to observe the phase appearance over different locations. In particular, the five mixtures of bio-oil/refinery intermediates were observed under Nikon ECLIPSE TE2000-S optical microscope. Three sets of analysis under optical microscope took place, to evaluate the homogeneity over different sample locations. Analytical characterization of HDT-Bio-oil and the most promising fossil-based candidate has been carried out and results have been compared.

RESULTS AND DISCUSSION

The miscibility of bio-oil with the 5 different refinery streams was comparatively assessed (Figure 1). Among the candidate refinery streams, FCC LCO was identified as the most compatible feedstock. The images of HDT- Bio-oil+LCO (30/70) sample were comparable to those of HDT-Bio-oil. Waxy, heavy compounds that exist in HDT-Bio-oil have been transferred to the mixture. Specifically, FCC LCO is the product of the Fluid Catalytic Cracking (FCC) unit, which is conventionally subjected to hydrotreatment (HDT) in order to reduce its sulphur levels and to saturate aromatics thus increasing its cetane number. Therefore, the present study further investigated the compatibility of LCO with BioMates towards downstream co-hydroprocessing, intended within existing petroleum crude oil refineries.

The study focused on feedstock investigations to show the potential technical bottlenecks for the hydrotreatment operation using the considered mixtures. The aforementioned potential technical constrains could be related to diffusion of reactants and products and catalyst pore blockage due to immiscibility and reactability effects leading to agglomerates formation.

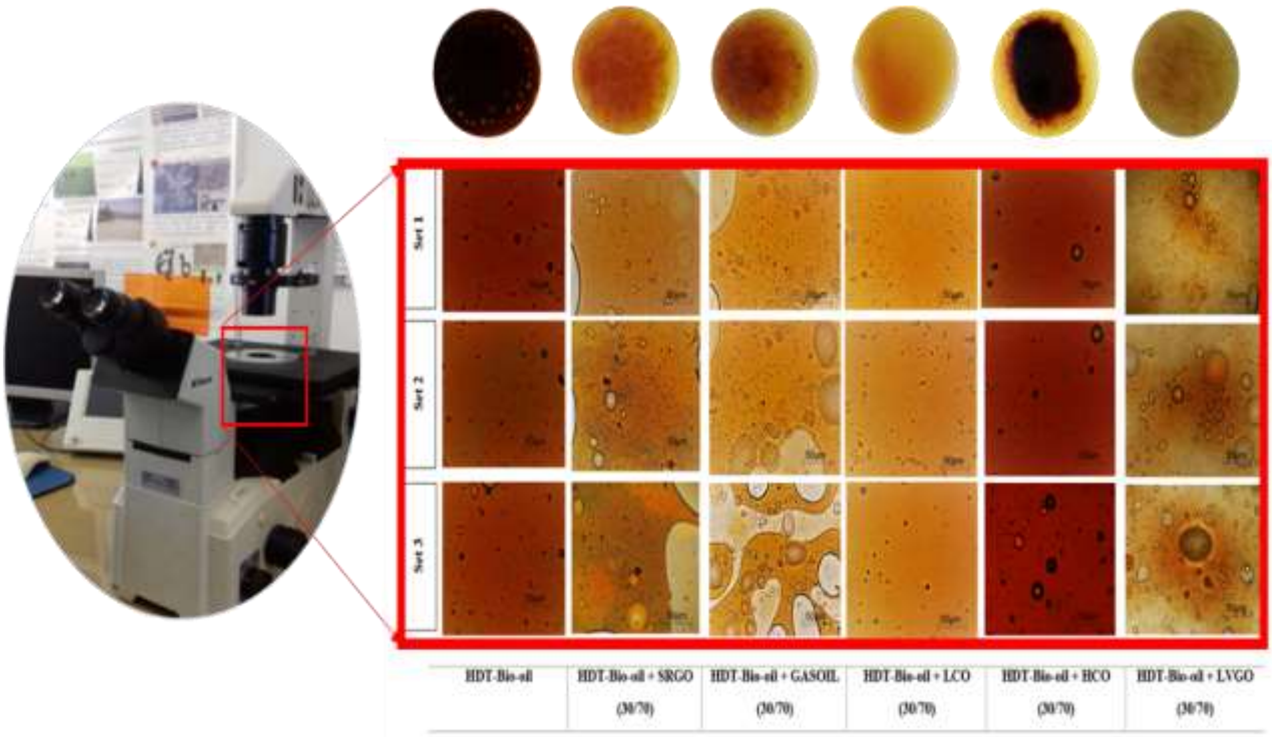

Figure 1: *Microscope analysis images of HDT-Bio-oil, selected petroleum fractions and their (30/70) mixture, respectively (magnification level for light microscopy images: 20; camera's magnification: 10). Source: Adopted from Manara et al., 2018, p. 311.*

On the basis of the experiments that were carried out in this study, a comparative assessment of possible refinery process locations for insertion of the HDT-Bio-oils is presented in Table 1.

Table 1*. Refinery integration comparative assessment*

Candidate entry points	Process unit	Remarks
FCC LCO	Hydroprocessing	Good miscibility. The binary blend presents increased homogeneity.
LVGO	Hydroprocessing	Quite good miscibility. Different phases attributed to dissolved water and mostly to hydrophobic, non-polar compounds.
FCC HCO	Hydroprocessing	Quite good miscibility. Agglomerates are formed that could cause catalyst blocking.
SRGO	Hydroprocessing	Quite bad miscibility. Different phases are formed. Not such a good candidate.
GASOIL	Hydroprocessing	Rather bad miscibility. Different phases and agglomerates are formed. Not a good candidate.

Table 2 presents the properties of HDT-Bio-oil, LCO (as received) and their (30/70) mixtures. HDT-Bio-oil resembles the properties of FCC light cycle oil (LCO). The experimental analyses of surface tension, density, viscosity, elemental composition, RI and boiling point distribution reveal good matches for the binary blend.
The refinery intermediate, FCC LCO, identified via this study as compatible with HDT-Bio-oil, will be further investigated via dedicated experimental testing on co-hydroprocessing. The study particularly targets to constitute a stepping stone towards further analyses and future directions for

hydrotreatment of candidate mixtures at continuous, industrially relevant processes. In particular, reaction pathways investigations and in detail multi-parameter hydrotreatment testing will formulate the operating window (e.g. temperature, pressure, catalyst) and finalize the proposed strategy for successful operation in industrially relevant environment. Although, the present miscibility assessment acts as pre-screening of candidate feedstocks for the targeted hydrogenation study that will follow-up, the study has potential other applications, taking into account refinery's requirements to process only homogenous mixtures/feedstocks.

Table 2: *Properties of HDT-Bio-oil, petroleum intermediates (as received) and their mixtures.*

Properties	Units	Method	HDT-Bio-oil	FCC-LCO	HDT-Bio-oil + LCO
Surface tension	dynes/cm	ASTM D1331	31.3	30.5	30.1
Density (15 °C)	kg/m3	ASTM D4052	1011.3	929.2	957.1
Kin. viscosity (40 °C)	cSt	D 445	45.4	6.9	
C	wt%		75.01	88.41*	84.41
H	wt%	ASTM	9.64	9.10*	9.32
N	wt%	D-5291	0.99	0.05*	0.29
O**	wt%		13.40	0.19	3.96
S	wt%	ASTM D 4294	0.96	2.25*	2.02
Water	wt%	ASTM D95	3.72		
RI		ASTM D1218	1.52	1.55	1.54

*Estimations based on BP data and literature.
**Calculated by difference.
Source: Adopted from Manara et al., 2018, p. 311.

The boiling range distributions for HDT-Bio-oil and LCO are presented in Figure 2.

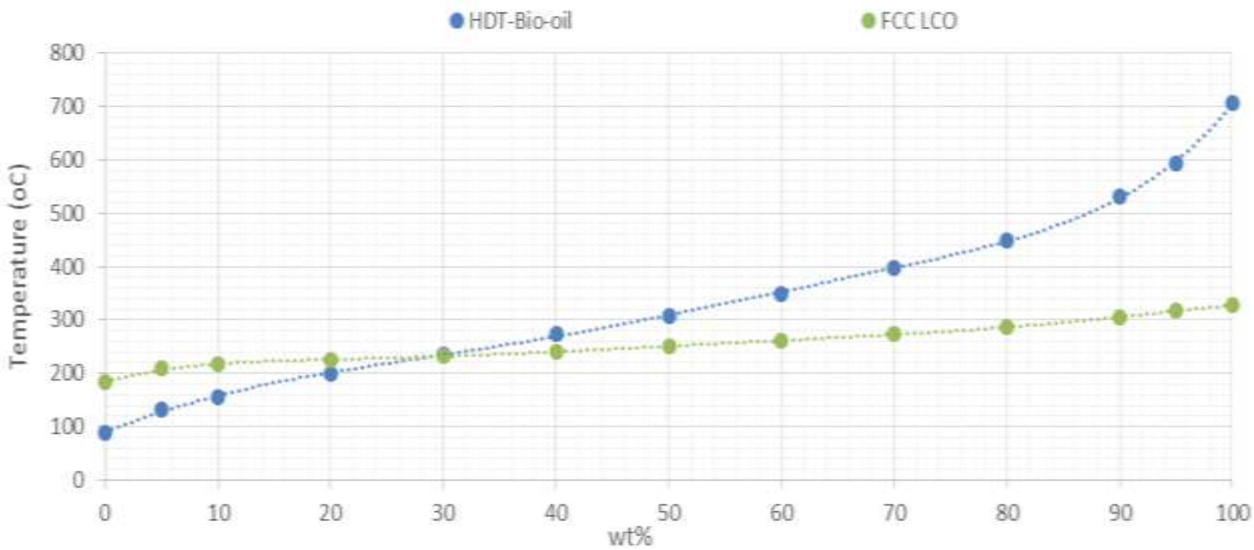

Figure 2: Distillation curve of HDT-Bio-oil and FCC LCO. Source: Adopted from Manara et al., 2018, p. 311.

CONCLUSIONS

The study investigates the phase behavior and properties of binary blends of bio-oil/fossil-based refinery intermediates in order to identify the appropriate refinery entry points and showcase the potential integration of bio-oils in the conventional refinery. In particular, the technological pathway under study concerns refinery integration of mild hydrotreated pyrolysis bio-oil.

FCC LCO was identified as the most compatible feedstock. The binary blend of HDT-Bio-oil and LCO presents increased homogeneity. Experimental analyses of density, viscosity, elemental composition, RI and boiling point distribution reveal good matches for the binary blend. HDT-Bio-oil resembles the properties of FCC light cycle oil (LCO). Likely to follow the same processing path as FCC LCO.

ACKNOWLEDGEMENTS

BioMates has received funding from the EU's H2020 research and innovation programme (grant agreement 727463). This abstract reflects only the authors' view. The agency INEA is not responsible for any use being made of the information it contains. Acknowledgements are also expressed to Prof. M. Moustaka and A. Stefanidou of Aristotle University of Thessaloniki, Greece, for their assistance in microscope analyses and to Prof. Karonis of National Technical University of Athens, Greece, for his assistance in the analytical characterization of samples. The authors would also like to thank Dr. David Kubicka of University of Chemistry and Technology Prague, Czech Republic, and Dr. Ulrich Pfisterer of BP Europa SE for providing the HDT-Bio-oil and refinery samples respectively.

LITERATURE

[1] EIBI, European Industrial Bioenergy Initiative. http://www.etipbioenergy.eu/?option=com_content&view=article&id=191.

[2] P. Manara, S. Bezergianni, U. Pfisterer. Energy Conversion and Management 165 (2018) 304–315.