BioMates

Public Summary of Deliverable D 3.7:
Report on technoeconomic validation of BioMates' refinery integration for hybrid fuels production

Version 01

Grant Agreement number:	727463
Project Acronym:	BioMates
Project title:	Reliable Bio-based Refinery Intermediates — BioMates
Start date of the project:	01/10/2016
Duration of the project:	31/03/2022
Deliverable N°.:	D55
Relative Deliverable N°.:	D3.7
Work Package N°. Task N°.:	WP3 (Task 3.5)
Deliverable title	Report on technoeconomic validation of BioMates' refinery integration for hybrid fuels production
Scheduled date of submission	28/02/2022
Date of submission of Version 01:	31/03/2022
Version:	01
Date of submission of this version:	31/03/2022
Dissemination Level:	Confidential, only for members of the consortium (including the Commission Services) **This summary: Public**
Project website address:	www.biomates.eu
The deliverable is elaborated on the basis of	Amendment – AMD-727463-25
Submitting party:	CERTH
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Reviewer:	David Kubička
Verification:	Report with public summary

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727463.

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1. Introducing BioMates

1.1. The BioMates Project

The BioMates project aspires in combining innovative 2nd generation biomass conversion technologies for the cost-effective production of *bio*-based inter*medi**ates* (BioMates) that can be further upgraded in existing oil refineries as renewable and reliable co-feedstocks. The resulting approach will allow minimisation of fossil energy requirements and therefore operating expense, minimization of capital expense as it will partially rely on underlying refinery conversion capacity, and increased bio-content of final transportation fuels.

The BioMates approach encompasses innovative non-food/non-feed biomass conversion technologies, including **ablative fast pyrolysis (AFP)** and single-stage **mild catalytic hydroprocessing (mild-HDT)** as main processes. Fast pyrolysis in-line-catalysis and fine-tuning of BioMates-properties are additional innovative steps that improve the conversion efficiency and cost of BioMates technology, as well as its quality, reliability and competitiveness. Incorporating **electrochemical H_2-compression** and the state-of-the-art **renewable H_2-production** technology as well as **optimal energy integration** completes the sustainable technical approach leading to improved sustainability and decreased fossil energy dependency. The overall BioMates-Concept is illustrated in Figure 1.

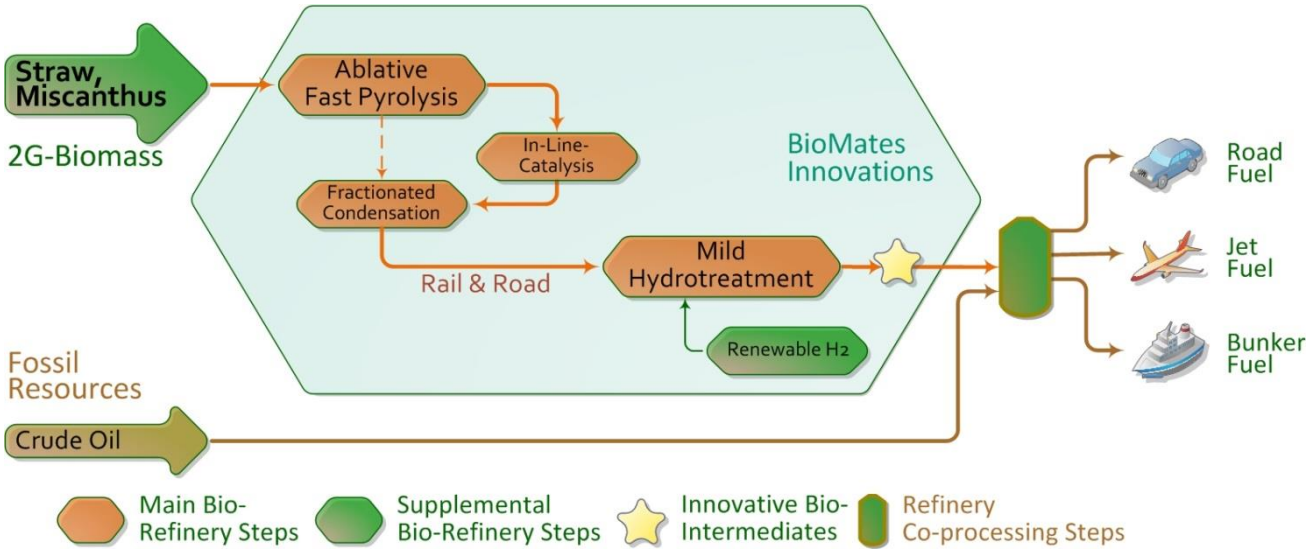

Figure 1: The BioMates-concept

The proposed technology aims to effectively convert residues and non-food/feed plants or commonly referred to as 2nd Generation (straw and short rotating coppice like miscanthus) biomass into high-quality bio-based intermediates (BioMates), of compatible characteristics with conventional refinery conversion units, allowing their direct and risk-free integration to any refinery towards the production of hybrid fuels.

1.2. European Commission support

The current framework strategy for a Resilient Energy European Union demands energy security and solidarity, a decarbonized economy and a fully integrated and competitive pan-European energy market, intending to meet the ambitious 2020 and 2030 energy and climate targets " /EC-2014a/EC-2014b/. Towards this goal, the European Commission is supporting the BioMates project for validating the proposed innovative technological pathway, in line with the objectives of the LCE-08-2016-2017 call /EC-2015/. Funding details are given in section 7 (p. 5).

1.3. The BioMates team

The BioMates team comprises nine partners from industry, academia and research centres:

- Centre for Research & Technology Hellas / CERTH - Chemical Process & Energy Resources Institute / CPERI, Greece (Project Coordination) - http://www.cperi.certh.gr
- Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Germany - www.umsicht.fraunhofer.de
- University of Chemistry and Technology Prague UCTP, Czech Republic - http://www.vscht.cz
- Imperial College London ICL, United Kingdom - www.imperial.ac.uk
- Institut für Energie und Umweltforschung Heidelberg gGmbH / ifeu, Germany - www.ifeu.de
- HyET Hydrogen B.V. / HyET, the Netherlands - www.hyethydrogen.com
- RANIDO, s.r.o., Czech Republic - http://www.ranido.cz
- BP Europa SE, Germany - www.bp.com/en/bp-europa-se.html
- RISE Energy Technology Center / RISE- www.ri.se

For additional information and contact details, please visit www.biomates.eu.

2. Preface

This report validates the BioMates process integration with existing petroleum refineries, as an alternative bio-based feedstock which can be co-fed directly, risk-free and without any additional infrastructure or limitations to conventional refinery operations. The main scope of this study is the production of 1000 L of hybrid fuel (partially fossil and partially bio-based origin) via co-hydroprocessing, which will be separated via the batch distillation pilot plant of CERTH allowing the production of a sufficient quantity of hybrid diesel and/or naphtha which will be employed for demonstration purposes as presented in WP7.

The following chapters of this report describe the BioMates end-use validation methodology (chapter 3), outlines the background corresponding actions (chapter 4 “BioMates end-use final products”) and presents the conclusions (chapter 5).

3. BioMates end-use validation methodology

The existing TRL5 hydroprocessing pilot plant HDS1 of CERTH /Bezergianni-2011/ was employed as a basis for the end-use validation of BioMates. Four testing runs in the TRL5 unit were conducted for the production of 1000L of hybrid fuel. The first preliminary three testing runs aimed at evaluating the most suitable petroleum fraction with which the BioMates can be blended, as well as on evaluating different ratios of petroleum fractions with BioMates and different reaction temperatures. The last dedicated testing run targeted to the production of a sufficient quantity of hybrid fuels, using the most suitable petroleum fraction and applying the most efficient operating conditions that were identified from the preliminary three testing runs. In addition to the production of 1000 L of hybrid fuel, over 100 L were fractionated for the production of the individual fractions of hybrid naphtha (Naphtha_CERTH_HyDis_S_BM[1]), kerosene (Kerosene_CERTH_HyDis_S_BM) and diesel (Diesel_CERTH_HyDis_S_BM) as final products from the BioMates project. The fractionation took place at the vacuum distillation unit HyDis of CERTH.

[1] Sample-codes of final BioMates-products; sample-codes of the intermediates are available at OpenAire, https://s.fhg.de/BioMates-OpenAIRE, tab “RESEARCH DATA”.

The produced BioMates from Task 3.3, reaching 180 liters, was used as co-feed with compatible fossil-based intermediates as defined and provided by BP. The Straight Run (atmospheric) Gas-Ooil (SRGO) and the Light-Cycle Oil (LCO) were selected as suitable petroleum-derived fractions for blending with BioMates in a ratio between 5 and 20 %vol. The LCO was initially selected as the most suitable candidate from a miscibility perspective (see D08 "Report on identification of BioMates refinery entry points candidates & specs"), but the BioMates produced in task 3.3 was proven that it is also miscible with the SRGO. /Manara-2018, Dimitriadis-2020/

A commercial $CoMo/Al_2O_3$ catalyst was utilized in all testing runs of co-processing, provided by BP as employed for hydrotreating of LCO in the refinery. In order to maintain a desired Liquid Hourly Space Velocity (LHSV), the catalyst was diluted with an inert material (silica carbide, SiC) to ensure that it would be effectively dispersed throughout the reactor for achieving good heat and mass transfer.

4. BioMates end-use final products

Co-hydroprocessing of BioMates with LCO at 5-20% v/v Biomates at 340-380 °C, 69 barg, Liquid Hourly Space Velocity (LHSV) of 1hr-1 and hydrogen to feed (H2/oil) ratio of 843 L/L was the feedstocks and conditions tested during the first run. The produced hybrid fuel (total liquid product) had 375-785 wppm S and 652-2500 wppm N, rendering optimal feedstocks the ones with the smaller BioMates content and optimal temperatures the highest ones.

Co-hydroprocessing of BioMates with SRGO/LCO at 10/90/60 v/v/v BioMates/SRGO/LCO relative ratios, as well as BioMates with SRGO at 10/90 v/v BioMates/SRGO ratio at 340-380 °C, 69 barg, LHSV=$1hr^{-1}$ and H2/oil=843 L/L was the conditions and feedstocks tested during the second run. The produced hybrid fuel exhibited 22-326 wppm S and 200-1000 wppm N, rendering optimal feedstocks the ones produced from co-hydroprocessing BioMates with SRGO (i.e. no LCO in the feed) and at higher temperatures.

Products from the 4^{th} and final testing run using Biomates/SRGO at 10/90 v/v ratio were collected and fractionated at CERTH, to obtain final hybrid end-fuel products, as presented in Figure 2. The indicative yields ranged between 11.9 – 16.5 % v/v for hybrid naphtha, 12.9-14.6 for hybrid kerosene, and 67.7-70.9 for hybrid diesel, while the heavier molecules ranged between 2.6-2.9 % v/v.

Samples of 5L of each hybrid end fuel type were shipped to BP where the end-fuels were analysed to determine their main fuel quality characteristics, pertinent for each fuel type, as well as biogenic carbon content based on ^{14}C measurements. The quality assessment of the hybrid naphtha sample indicated that the produced end-fuel abides by the corresponding EN 228 specifications. The only properties that were outside the naphtha specification ranges were density and paraffins content. The hybrid kerosene quality assessment showed that the produced end-fuel abides by the corresponding ASTM D1655 specification. The only properties that were outside the jet fuel specification ranges were sulfur content and freezing point Finally, the quality assessment of the hybrid diesel sample confirmed that the end-fuel abides by the EN590 specifications, with the exception of sulphur and aromatics content.

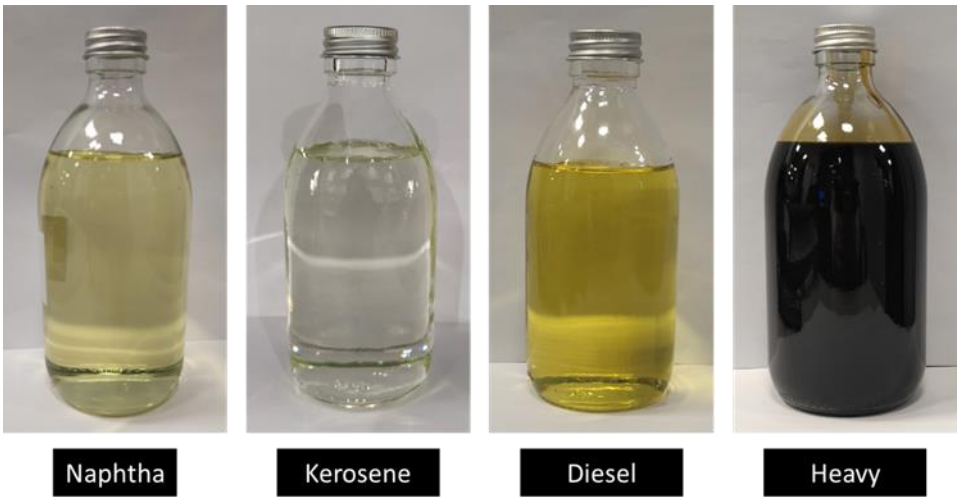

Figure 2: Fractions of hybrid naphtha, jet fuel, diesel and heavy residue

According to the ^{14}C measurements that were carried on the three hybrid fuels, one can estimate from activities a bio content of naphtha of 27 %, of kerosene of 14 % and finally of diesel of 6.5 %.

5. Conclusions

The intended BioMates end-use is evaluated and presented in this report. More specifically, BioMates potential integration in underlying refineries is evaluated by performing co-hydroprocessing test runs with different refinery fossil-based intermediate fractions. For the end-use validation, the TRL5 hydroprocessing pilot plant and vacuum distillation units of CERTH were employed.

Over 1000 L of hybrid fuels were produced by co-hydroprocessing the available 180L of BioMates with Straight Run Gas-oil (SRGO), Light Cycle Oil (LCO) and their blends at different hydroprocessing temperatures and at constant system pressure, Liquid Hourly Space Velocity (LHSV) and H_2/oil ratio. BioMates was used as a co-feed at 5-20 % v/v range with the fossil counterparts utilizing commercially available $CoMo/Al_2O_3$ hydrotreating catalyst that is used for hydrotreating the fossil fractions in the underlying hydrotreating plants. Over 100 L of hybrid fuels were fractionated at CERTH's vacuum distillation unit to produce final hybrid fuel end-products, i.e. hybrid naphtha, hybrid kerosene and hybrid diesel, in order to technically evaluate their quality characteristics and biogenic carbon content.

The quality assessment of hybrid naphtha, hybrid kerosene and hybrid diesel were conducted by BP, which concluded that the three end-products abide for the most part to the corresponding fuel standards (EN228, ASTM D 1655 and EN590 respectively). According to the ^{14}C measurements that were carried on the three hybrid fuels, one can estimate from activities a bio content of naphtha of 27 %, of kerosene of 14 % and finally of diesel of 6.5 %.

6. Disclaimer

This Deliverable report reflects only the authors' view; the European Commission and its responsible executive agency CINEA are not responsible for any use that may be made of the information it contains.

7. Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727463.

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