BioMates

Public Summary of Deliverable D 2.2:

Report on identification of BioMates refinery entry points candidates & specs

Version 01

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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.

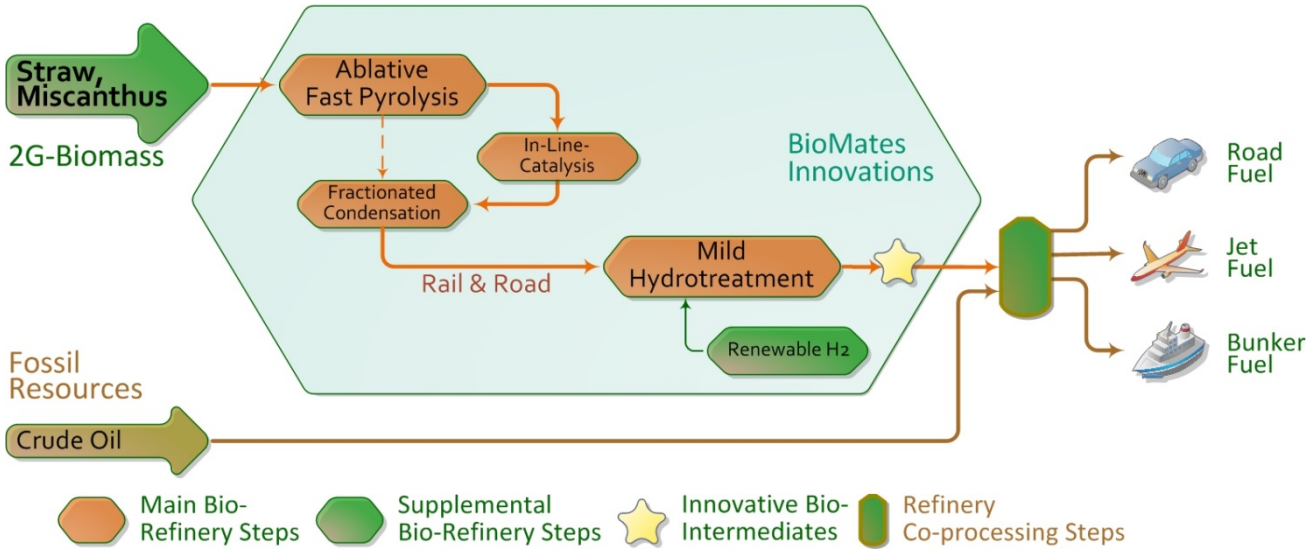

Figure 1: The BioMates-concept

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/. This

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

1.3. The BioMates team

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

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

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

2. Preface

Within the BioMates project, there is a dedicated task, numbered Task 2.2 and called "Task 2.2: Optimization of mild-hydrotreatment upgrading integration with refinery" that focusses on the interfaces between intermediates production and their later usage in refineries.The confidential deliverable D2.2. "Report on identification of BioMates refinery entry points candidates & specs" provides an assessment of the technical activities related to the objectives of this Task 2.2 and, in general of the whole work package 2 "Innovative bio-oil upgrading for refinery integration".

The potential of identifying refinery compatible Entry Points to directly co-feed bio-based refinery intermediates, BioMates, and further co-processing them in existing petroleum crude oil refineries is investigated. The report was carried out by a BioMates working group, led by CERTH and BP. A brief introduction of the technical goals of this study and the employed methodological approach is initially provided in section 3. In section 4, BioMates and fossil-based refinery intermediates properties are juxtaposed to identify potential fossil-based candidates for co-processing. The miscibility of the aforementioned renewable and conventional fuels and conclusions as well are presented in sections 5 and 6, respectively.

3. Introductive methodological approach

The aim of the study lies within the general objective of the BioMates project to develop cost-competitive sustainable bio-fuels for today's transportation infrastructure. The project aspires to overcome techno-economic limitations associated with valorising pyrolysis bio-oil as an alternative fuel, by developing and validating an innovative technological pathway of producing (via ablative fast pyrolysis) and upgrading (via mild catalytic hydrotreatment) 2G-biomass bio-oil as well as its integration into an existing refinery.

Pyrolysis bio-oil is a mixture of oxygenated compounds. The heteroatom distribution in pyrolysis bio-oil differs from the characteristic of petroleum refinery fuels and therefore affects co-processing. All these properties make the direct co-processing of pyrolysis oil itself in standard refinery units at least problematic. Several pyrolysis process modifications are currently being studied to obtain bio-oils of improved quality. Nevertheless, conventional pyrolysis bio-oil requires upgrading aiming to reduce oxygen and water content and thus acidity, enabling co-processing without the need for major refinery modifications. Within the BioMates project, upgraded pyrolysis bio-oil is evaluated as a potential refinery co-processing feedstock. In particular, mild hydrotreatment (HDT) of pyrolysis bio-oil was applied in order to upgrade pyrolysis bio-oil, fulfil specifications and become a "drop-in" biofuel in compatible refinery "location". Several studies can be found in the contribution, regarding bio-oil co-processing with petroleum fractions. However, limited research works focus on identifying suitable refinery intermediates co-feeds. Therefore, in order to identify the appropriate refinery entry point, i.e. specific process unit(s) within the refinery, the following tasks have been conducted as part of the BioMates methodology:

A. Comparison of bulk fuel properties of BioMates with those of refinery streams.

B. Assessment of miscibility between BioMates and refinery intermediates.

The compatible pairs of refinery intermediates and BioMates identified via this study will be investigated further in WP2 via dedicated experimental testing (TRL 3[1]).

4. Refinery entry point candidates and specifications

Refinery intermediates' characteristics from the industrial partner BP served as the basis for the produced BioMates quality targets. The analysis was based on the bulk properties, mapping several petroleum fractions' properties (i.e., boiling curves, gravities/densities, overall elemental compositions) within a conventional refinery. The properties of the various refinery fractions, i.e. potential BioMates "Entry Points" were juxtaposed with the properties of produced BioMates at different operating conditions, focusing on those comparable to refinery intermediates' properties. Based on the results of juxtaposition of the different BioMates and refinery intermediates' properties (density, distillation data, and stoichiometric composition) the following refinery streams have been identified as compatible, potential candidates for co-processing with BioMates:

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

5. Miscibility experimental assessment

Refinery intermediates and mild-hydrotreated bio-oil (BioMates) 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

[1] According to Annex G of the HORIZON 2020 WORK PROGRAMME 2016– 2017, Technology readiness level (TRL) 3 is defined as "experimental proof of concept".

leading to agglomerates that can prohibit catalytic hydroconversion. Furthermore, analytical characterization of the samples has been carried out and results have been compared.

5.1. Materials preparation

Fossil-based refinery intermediates from project partner BP and upgraded bio-oil from UCTP were delivered to CERTH in order to study BioMates possible refinery entry points and specs for the purposes of Deliverable D2.2. The miscibility of the HDT-bio-oil/refinery intermediates was examined by preparing a set of binary bio-oil/ refinery intermediates mixtures, using the five pre-selected refinery streams and 30 vol.-% bio-oil. In particular, the following mixtures have been prepared:

a) HDT-Bio-oil + SRGO (30/70),
b) HDT-Bio-oil + GASOIL (30/70),
c) HDT-Bio-oil + FCC LCO (30/70),
d) HDT-Bio-oil + FCC HCO (30/70),
e) HDT-Bio-oil + LVGO (30/70).

5.2. Phase behaviour of HDT-bio-oil/refinery intermediate binary mixtures

The miscibility of two streams was measured as the homogeneity of the mixture. The homogeneity of HDT bio-oil/refinery intermediates binary systems was investigated via light microscopy. The five mixtures of bio-oil/refinery intermediates were observed under Nikon ECLIPSE TE2000-S optical microscope in order to comparatively assess the homogeneity of the mixtures. The typical magnification level used for light microscopy images was 20, while camera's magnification was 10, resulting in total magnification of 200. The different samples were microscopically "scanned" in order to observe the phase appearance over different locations. The following descended order for miscibility was identified: LCO> LVGO> HCO> SRGO> GASOIL.

5.3. Fuel properties evaluation

According to the needs of the present study, a portfolio of analytical methods was applied to the samples, as received, and, furthermore, to the selected bio-oil/refinery intermediates mixtures. The density of the fuels (kg/m^3) was measured via ASTM D4052. The surface tension of fuels samples (dynes/cm) was determined via ASTM D1331. Surface tension measurements were carried out at room temperature (~25 °C). The heteroatom distribution (wt% oxygen, nitrogen and sulphur content) was conducted based on ASTM D-5291 and ASTM D4294. Viscosity has been defined based on ASTM D 445. Refractive Index is determined based on ASTM D1218. Finally, distillation analysis was based on ASTM D 6352. Based on the analytical characterization results, a comparative analysis showed that BioMates resemble the properties of FCC LCO, LVGO and finally FCC HCO and could follow the same processing path.

6. Refinery integration concluding remarks

The BioMates project technology scale up and validation in TRL-5 in the intended simulated environment that renders reliable late-stage research operation data necessitated a miscibility study to identify BioMates compatibility with refinery's intermediates. Taking into account the miscibility assessment of HDT-bio-oil/refinery intermediate binary mixtures, and in particular, the phase behaviour of the binary mixtures and the produced fuels properties, first FCC LCO and secondly LVGO have been concluded to be the most promising candidates for co-processing, resembling HDT-bio-oil's properties.

7. Disclaimer

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

8. Literature

EC-2014a European Commission, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions - A policy framework for climate and energy in the period from 2020 to 2030, COM(2014) 15 final, Brussels, 22.1.2014, http://www.europarl.europa.eu/meetdocs/2009_2014/documents/nest /dv/depa_20140212_06/depa_20140212_06en.pdf; *http://bit.ly/1LUcJKL*

EC-2014b European Commission, Energy Union Package - Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions and the European Investment Bank - A Framework Strategy for a Resilient Energy Union with a Forward-Looking Climate Change Policy, COM(2015) 80 final, Brussels, 22.1.2014,http://eur-lex.europa.eu/resource.html?uri=cellar:1bd46c90-bdd4-11e4-bbe1-01aa75ed71a1.0001.03/DOC_1&format=PDF, *http://bit.ly/198SAUf*

EC-2015 European Commission, LCE-08-2016-2017 "Development of next generation biofuel technologies", Publication date: 14 October 2015, https://ec.europa.eu/research/participants/portal/desktop/en/opportunities/h2020/topics/lce-08-2016-2017.html, *http://bit.ly/2ndtvPc*