BioMates

Public Summary of Deliverable D 2.6:

Report on optimal mild-HDT operation of AFP bio-oil upgrading

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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, minimisation 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.

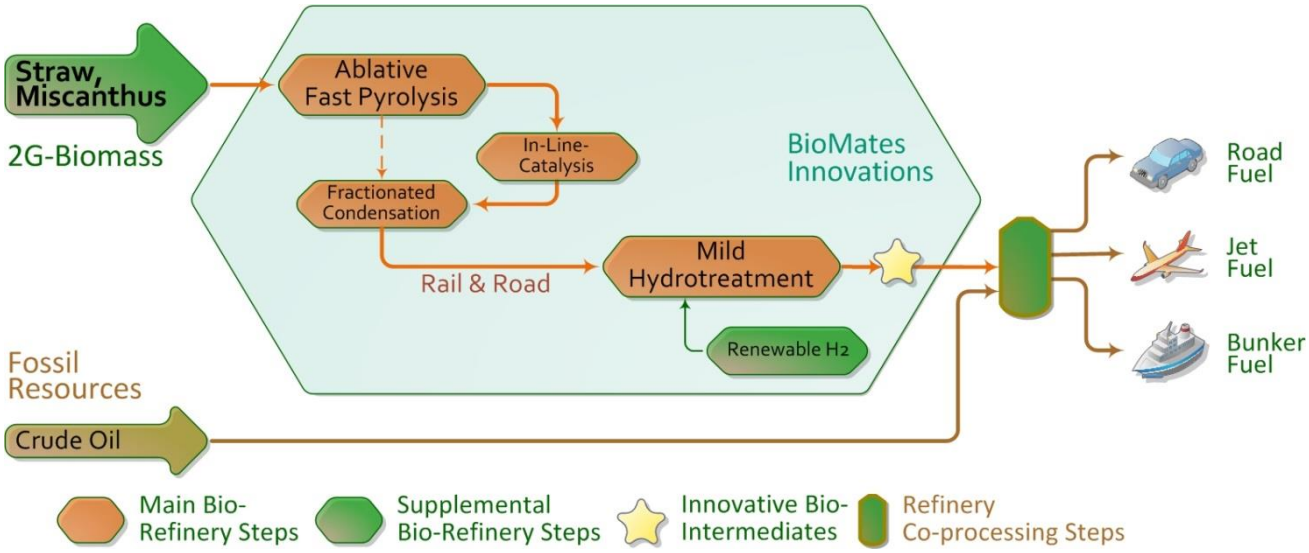

Figure 1: The BioMates-concept

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 decarbonised 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 - *www.cperi.certh.gr*
- University of Chemistry and Technology Prague, Czech Republic - *www.vscht.cz*
- Imperial College London, United Kingdom - *www.imperial.ac.uk*
- Institut für Energie und Umweltforschung Heidelberg GmbH / ifeu, Germany - *www.ifeu.de*
- HyET Hydrogen B.V. / HyET, The Netherlands - *www.hyethydrogen.com*
- RANIDO, s.r.o., Czech Republic - *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

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, rendering necessary an upgrading step for bio-oil. In particular, mild hydrotreatment (HDT) of pyrolysis bio-oil is studied as the main upgrading step of pyrolysis bio-oil targeting to its conversion to a compatible feedstock that can be integrated without any risk within a common refinery complex.

The BioMates project's "Task 2.2: Optimisation of mild-hydrotreatment upgrading integration with refinery" focuses on the evaluation of the mild-HDT process as the proposed pathway to upgrade AFP bio-oil as a reliable bio-based refinery intermediate (BioMates). Moreover, this Task encompasses some preliminary testing of co-hydrotreating BioMates with the optimal refinery fraction as identified in the deliverable "D2.2 Report on BioMates refinery entry points & specs". For this confidential deliverable, a public summary is available, and more information in meanwhile published by Manara et al. /BioMates-D2.2PS/Manara-2018/

The confidential deliverable "D2.6 Report on optimal mild-HDT operation of AFP bio-oil upgrading", that this Public Summary is based upon, reports the experimental testing results of the two aforementioned studies; this Public Summary reports the basics of the non-confidential content.

3. Methodology

Both mild-HDT of AFP bio-oil for BioMates production and co-processing BioMates with a suitable petroleum fraction were tested in the TRL3 hydroprocessing pilot plant of CERTH. This hydroprocessing pilot plant works in the nominal operating window of an industrial scale hydroprocessing unit (range of reactor temperature, system pressure, H2/oil ratio). For the mild-HDT testing, 50 L of straw[1]- and 50 L of Miscanthus-based AFP bio-oil were used as the main feedstock, which were provided by Fraunhofer-UMSICHT. Both were produced comprising staged condensation according to the procedure described in Deliverable D1.2 /BioMates-D1.2/. Furthermore, several samples of the custom-made hydrotreating catalyst produced by Ranido were used as the main catalytic system of the experiments. All products were analysed via CERTH analytical laboratory.

The preliminary co-processing test runs were conducted by utilising the products of the mild-HDT test runs (BioMates) together with a suitable refinery co-feedstock, identified under the same Task 2.2 (see "D2.2 Report on identification of BioMates refinery entry points candidates & specs"), and provided by BP. Furthermore, the operating window and catalytic system for co-processing were provided by BP. All products were analysed via CERTH analytical laboratory.

4. Defining optimal operating window of mild-HDT of AFP bio-oil

Two types of AFP bio-oil were tested as mild-HDT feedstocks, straw- and miscanthus-based bio-oil, both provided by Fraunhofer-UMSICHT, while employing a custom-made catalyst provided by Ranido.

Straw-based bio-oil mild-HDT runs evaluated different reactor temperatures (300-360 °C), system pressure (580 - 1,000 psig[2]) and H_2/oil ratios (3,000 - 5,000 scfb[3]). The different operating parameters were tested via a comprehensive yet compact experimental protocol, allowing an evaluation of the effect of each one of these parameters on the overall process effectiveness. The evaluation basis that all conditions were compared for was

- the effect of each set of conditions on the pressure drop build up,
- the middle distillate (and primarily diesel) yield,
- HDO (hydrodeoxygenation) effectiveness,
- reduction of TAN (total acid number) and
- reduction of H_2 consumption.

Miscanthus-based bio-oil mild-HDT runs were too short to provide a comprehensive evaluation of the effectiveness of different process conditions. In particular, it was observed that the pressure drop build-up was too fast to maintain steady-state operation, and within a few hours, the catalytic system was clogged, indicating the presence of particles. Several testing runs were attempted including tests with different reactor temperatures (300 - 360 °C) and H2/oil ratios (5,000 - 10,000 scfb), all leading to the same results. This problematic behaviour of Miscanthus-based bio-oil was also observed in parallel hydroprocessing tests at UCTP, indicating that the quality characteristics of Miscanthus-based AFP bio-oil are unsuitable for mild-HDT upgrading with respect to the custom catalyst and operating window identified in the project. However

[1] A mixture of barley- and wheat-straw, 50/50 m/m

[2] As this work is strongly refinery-correlated, the pressure unit commonly used in refinery industry is chosen (pound-force per square inch – psi, 1 psi = 6,895 Pa)

[3] Standard cubic feet per barrel, the common unit in refineries for this ratio (1 scfb = 0.1781 m^3/m^3)

Miscanthus-based bio-oil will be explored further in TRL5 (WP3), as scaling up might improve the quality of bio-oil produced and downstream upgrading potential.

5. Preliminary BioMates refinery integration potential testing

The mild-HDT straw-based bio-oil (BioMates) produced via the aforementioned testing within the same Task, was employed for the preliminary co-hydroprocessing experiments as the bio-based co-feed. Light Cycle Oil or LCO, as it was identified as the most compatible refinery /BioMates-D2.2PS/Manara-2018/, was the fossil-based co-feed employed for the preliminary co-hydroprocessing tests, which was provided by BP. All preliminary co-hydroprocessing testing were conducted in the aforementioned CERTH's TRL3 hydroprocessing pilot plant and for all the tests, the catalyst was a commercial LCO hydrotreating catalyst that was provided by BP. Three BioMates – LCO blending ratios were evaluated, namely 10/90, 20/80 and 30/70 v/v, within a specific operating window defined by the nominal operation of a typical LCO hydrotreating process.

All in all, the proposed technology renders a promising intermediate for co-hydroprocessing with petroleum-based fractions like LCO. In particular, the HDO bio-oil is an intermediate feed of excellent ignition quality that could be integrated without any significant technical problem within a typical refinery. The successful oxygen- and water-content-reduction from the initial straw-based bio-oil feed via the proposed mild hydrotreating process render this technology a very promising way to upgrade and promote the use of bio-oil for fuel production. Several fuel properties of the upgraded HDO bio-oil are improved, as the initial viscosity, TAN and density are all reduced to a great extent. The results have shown that mild hydrotreating conditions are the preferable conditions both from product-quality- and process-performance-point of view.

6. 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.

7. Literature

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