BioMates

BioMates validation via mild-HDT + RES-based make-up H2

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1. Preface

1.1. Introducing BioMates

The BioMates project aims to combine innovative 2nd generation biomass conversion technologies for cost-effective production of bio-based intermediates (BioMates) that can be further upgraded in existing oil refineries as renewable and reliable co-feedstocks as shown in Figure 1. The BioMates approach covers innovative biomass (straw and miscanthus) conversion technology, including ablative fast pyrolysis (AFP) and single-stage mild catalytic hydroprocessing (mild-HDT) as main conversion processes. Up until now, the AFP and mild-HDT technologies have been developed (WP1 and WP2 respectively), while the AFP technology has also been validated in TRL5 industrially relevant environment (WP3, Tasks 3.1 and 3.2).

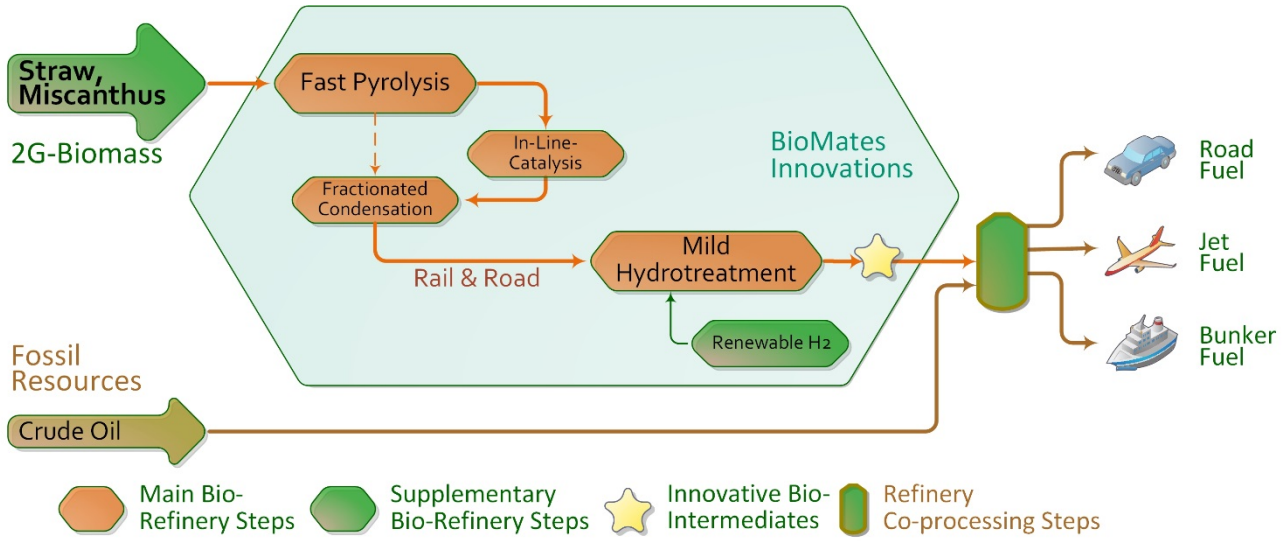

Figure 1: The BioMates-concept

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 nine 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 UCTP, Czech Republic - *http://www.vscht.cz*
- Imperial College London ICL, United Kingdom - *www.imperial.ac.uk*
- Institut für Energie und Umweltforschung Heidelberg GmbH / ifeu, Germany - *www.ifeu.de*
- HyET Hydrogen 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
- RISE Research Institutes of Sweden - www.ri.se

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

1.4. TRL5-AFP bio-oil upgrading

This report presents the progress on validating in TRL5 the AFP bio-oil upgrading via mild-HDT incorporating RES-based make-up H_2 as part of the ongoing Task 3.3 "Lab- to pilot-scale mild-HDT incorporating RES-based make-up H_2 for BioMates production". This report is organized in the following sections: a) an introduction (section 2) where the background corresponding actions are outlined, b) the methodology description including the bio-oil characteristics, TRL5 plant description and validation plan (section 3), c) the presentation of the current results (section 4), and finally d) conclusions and next steps (section 5), as the action is on-going.

2. Introduction

The BioMates 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 which enables cost reduction of bio-oil production and bio-oil properties improvement. The BioMates approach encompasses innovative non-food/feed biomass conversion technologies, including ablative fast pyrolysis (AFP) and single-stage mild catalytic hydrotreatment (mild-HDT) as main processes. AFP in-line-catalysis and fine-tuning of BioMates properties are additional innovative steps that improve the conversion efficiency and cost of the overall BioMates technology, as well as its quality, reliability and competitiveness. Incorporating 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 targeted BioMates will have compatible characteristics with conventional refinery conversion units, allowing their direct and risk-free integration to any refinery towards the production of hybrid fuels.

The AFP has been developed in TRL4 (WP1) and validated in TRL5 (WP3) upon the TRL5 plant adjustment (see submitted deliverable D3.1/D18 "1st batch for mild-HDT produced"). The AFP validation was confirmed by the production of over 1000 kg of bio-oil via the TRL5 AFP plant (see submitted deliverable D3.2/D23 "Bio-oil, validating AFP"). The AFP bio-oil upgrading via mild-HDT was developed in WP2 at TRL3. Instrumental to the development was the mild-HDT catalyst development (see submitted deliverable D2.1/D07 "Development of custom made hydrotreating catalyst"), which provided a suitable and effective catalyst that enables the bio-oil hydrotreatment under the mild-HDT operating conditions targeted (Dimitriadis-2020). The identification of the optimal operating parameters that allow effective conversion of bio-oil to BioMates rendered an effective conversion step (see submitted deliverable D2.6/D30 "Report on optimal mild-HDT operation of AFP bio-oil upgrading"), which achieved over 95% oxygen removal, acidity reduction to negligible values, and diesel yield increase over 30% (wt%) over the AFP bio-oil. Furthermore, instrumental to the mild-HDT technology is the

development of an innovative electrochemical hydrogen compressor and purifier system (see D2.3/D13 "Report on the electrochemical hydrogen compressor and purifier performance during validation testing"), intended to be integrated with the mild-HDT TRL5 plant during the validation.

The scope of the current deliverable is the validation of the AFP bio-oil upgrading via mild-HDT in TRL5, employing the custom-made catalyst identified (see D2.1/D07) and optimal mild-HDT operating window determined (see D2.6/D30). Furthermore, the mild-HDT TRL5 validation will also include electrochemical hydrogen compression and purification of the recycled (not reacted H_2), while the make-up H_2 will be provided by an underlying solar based water electrolysis system.

The first version of this report was submitted timely on 23.12.2020. Afterwards, an amendment request was granted. The report was requested by the consortium to be reopened in order to submit a revised version, considering the adaptions granted via the amendment and some updates.

3. Methodology

The AFP bio-oil conversion to BioMates via the integrated mild-HDT + RES-based H_2 in TRL5 envisions several steps. Firstly, the TRL5 AFP-bio-oil from RISE and custom-made hydroprocessing catalyst from Ranido are sent to CERTH. The quality characteristics of the TRL5 bio-oil are compared with the ones of the TRL4 bio-oil performed when WP1 was ongoing at UCTP, using the analytical methodology developed under WP1. Secondly, the TRL5 validation infrastructure at CERTH is prepared, considering the necessary upgrading/revamping of underlying systems, the development of new systems, as well as the testing of the TRL5 systems and subsystems to confirm operability. Thirdly, preliminary tests are conducted with the TRL5 bio-oil in the underlying TRL3 mild-HDT plant to harmonize the outputs of WP2 towards the TRL5 validation in WP3. Finally, the TRL5 AFP-bio-oil is fed to the TRL5 mild-HDT pilot plant at CERTH, which includes the integration of the EHC and EHP system, while the make-up H_2 is used to compensate for the H_2 consumed is provided by the underlying RES-based H_2 production facility at CERTH.

The validation in TRL5 has to allow the up-scale of both mild-HDT and EHC/EHP systems, their integration, and very importantly the harmonization of the operation with the TRL5 AFP bio-oil, which has key quality differences from the WP1-bio-oil that the technology was developed and tested with in TRL3 in WP2. As a result, preliminary tests in TRL3 of the EHC/EHP system and its integration with the mild-HDT were performed in 4Q2019 and 4Q2020, validating its operation and effectiveness. Subsequently, preliminary tests of the TRL5 bio-oil in the mild-HDT TRL3 plant were performed in 2Q2020 and 3Q2020, when the unforeseen first COVID-19-wave lockdown interrupted operation of the validation site at CERTH. Finally, validation of the BioMates production started in November 2020 employing TRL5 bio-oil as feed for the TRL5 mild-HDT plant at CERTH.

4. Results

Upon harmonization tests of mil-HDT of TRL5 bio-oil via the TRL3 mild-HDT plant integrated by the EHC/EHP system, the technology was scaled up in the upgraded TRL5 mild-HDT plant. The validation involved the custom-made catalyst developed by Ranido and tested in WP2, and the mild-HDT conditions identified as optimal in WP2 via TRL3 tests. Eight (8) TRL5 mild-HDT production tests were performed leading to the production of a total liquid product, which consisted of an organic phase product (BioMates) and an aqueous

phase product. Since the delayed start of the validation, 180 l of organic phase product, i.e. BioMates was produced, while the aqueous phase produced accounted of 5.1-20.8 wt% of the total liquid product. The average BioMates product yield of the mild-HDT was 79-81 %vol.

Significant improvement has been achieved over the starting bio-oil properties. The density of the initial bio-oil was reduced from 1.045 to ~0.95 g/ml showing that cracking reactions of the heavy molecules were successful. Furthermore, the sulfur content was reduced from 3270 wppm (bio-oil + DMDS) to 52-110 wppm due to the successfulness of hydrodesulfurization reactions. The oxygen content, as well as the dissolved water of the initial bio-oil, were removed via hydrodeoxygenation reactions leading, to an organic phase product with significantly reduced oxygen (<5.6 wt%) and dissolved water (<1 wt%) content. Finally, significant improvements were also achieved in viscosity which was reduced to <25 cSt and total acid number – TAN – which reached negligible levels. In general, it was validated in TRL5 that the AFP bio-oil hydrotreatment renders a high-quality organic phase liquid product with low density, high carbon and hydrogen content, negligible oxygen as well as water content and improved viscosity and TAN, properties that allow its potential use as a refinery co-feed.

Figure 2: Two -phase product from bio-oil hydrotreatment of RUN-03

The TRL5 validation also included the integration of HyET's Electrochemical Hydrogen Compressor (EHC) and Electrochemical Hydrogen Purififcation (EHP) system which successfully enabled purification and recycling of a portion of the H2 contained in the mild-HDT gaseous product.

5. 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.

6. Literature

Dimitriadis-2020 Dimitriadis A, Chrysikou L, Meletidis G, Terzis G, Auersvald M, Kubička D, Bezergianni S, Bio-based refinery intermediate production via hydrodeoxygenation of fast pyrolysis bio-oil, *Renewable Energy* 168, pp. 593-605, 2021 [DOI: 10.1016/j.renene.2020.12.047]

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, 22.01.2014, 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, 22.01.2014, 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*