Fuels from Reliable Bio-based Refinery Intermediates – *BioMates*

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Summary

The BioMates technology aims to convert residues and 2G-biomass like straw and miscanthus into high-quality bio-based intermediates (the "BioMates"), of compatible properties with conventional refinery conversion units, allowing their direct and risk-free integration to any refinery towards the production of hybrid fuels. The BioMates approach encompasses innovative non-food/non-feed biomass conversion technologies, including ablative fast pyrolysis (AFP) and single-stage mild catalytic hydrotreating (mild-HDT) as main processes. In-line-catalysis and staged condensation in AFP as well as electrochemical H_2-compression in mild-HDT are additional innovative steps that improve the conversion efficiency and product quality of the BioMates approach. BioMates is a Horizon 2020-project, put into practice by eight partners from industry, academia and research centres. First results: Bio-oil production from wheat straw in a TRL 4 AFP-plant (meant for catalyst development) was performed with a yield of 21 wt.-%. Mild-HDT of such bio-oil lead to organic product phases with acid numbers down to 3.0 mg_{KOH}/g_{Sample} for reaction temperatures of up to 360 °C.

1. Introduction and Approach

To date, road fuels are almost exclusively provided by blending fossil fuels from refineries with separately manufactured biofuels at the end of both processes. There are some conventional refineries co-feeding vegetable oils in Europe, but since bio-oils' properties are incompatible with the conventional refinery processes this is only possible at very low level. For future large-scale co-feeding of bio-based material into refineries (instead of blending after the refinery processes), well-defined co-feed material would be essential. This is where "BioMates", a project funded by the European Union's research and innovation programme Horizon 2020, comes into play.

Having started in October 2016, the project aims at manufacturing intermediate products made from wood-like or stalk-like non-food biomass, e.g. from agricultural residues. Such bio-based intermediates will be highly suitable for direct integration in a conventional oil refinery. The cost-effective and decentralized valorisation of residual and non-food biomass (like straw and the perennial grass *Miscanthus x giganteus*) for the production of bio-based products is a key element of the project. The fossil-dominated refining sector could utilise a bio-based co-feed of reliable properties in existing conversion units. Hybrid fuels with a high bio-based content, fully compatible with conventional combustion systems, would be the output.

Of course, co-feeding cellulosic-biomass-derived intermediates into conventional refineries strictly requires compatibility of the intermediates with the refining process and, especially, the reliability of the intermediates' properties. In the end, fuel qualities meeting the standards and fuel yields not diminished by intermediate-caused off-spec batches are the explicit goal.

This defines the idea behind the BioMates-concept (Fig. 1): a fast pyrolysis converts lignocellulosic feedstock to bio-oil which is upgraded to a high-quality bio-based intermediate to be readily co-fed in a conventional refinery. The first step involves ablative fast pyrolysis (AFP), optionally enhanced by in-line-catalysis in the AFP-reactor to optimise the bio-oil with respect to the later refinery application. In a second step (optionally at another location), mild hydrotreatment (mild-HDT) upgrades the AFP bio-oil into intermediates with reliable properties to be fed into refineries. Applying solar-generated renewable make-up hydrogen and electrochemical compression of the recycled gas improves further the carbon footprint and production costs of the bio-based intermediates.

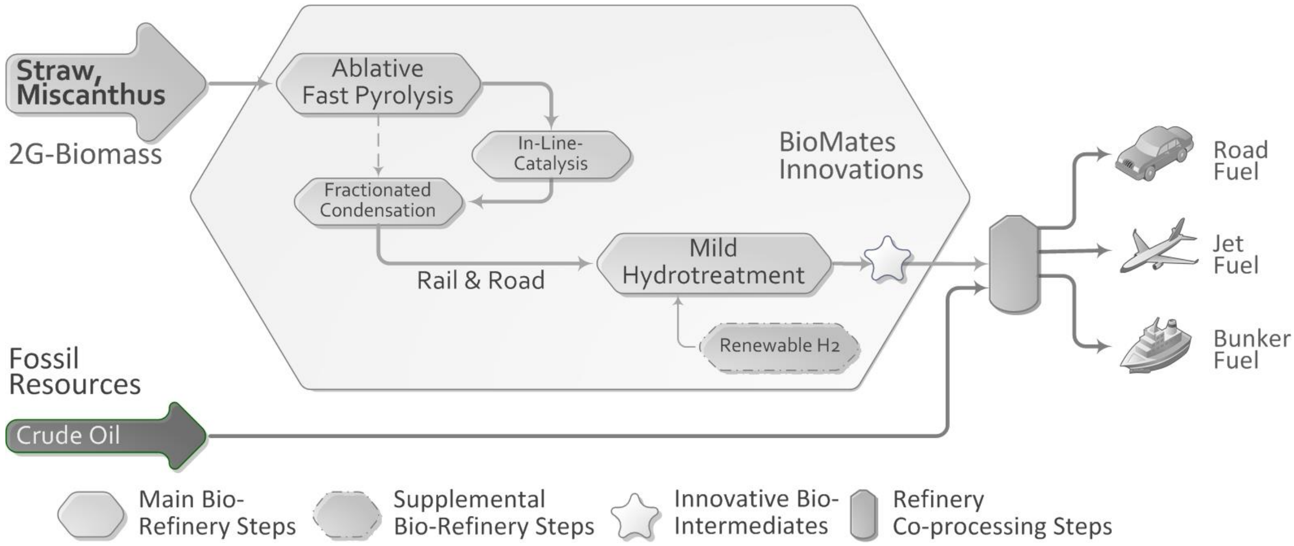

Fig. 1: Schematic illustration of the BioMates concept to produce bio-based intermediates for co-feeding in conventional refineries

2. Methods and scales

The proposed pathway for decarbonisation of transport fuels will be validated via so-called TRL 5-units, where Technological Readiness Level (TRL) 5 indicates technologies that are validated in an industrially relevant environment[1]. This will allow the development of an integrated, sustainability-driven business case encompassing commercial and social aspects for the exploitation strategy. Prior R&D will be done in TRL 4-plants, denoting technologies validated in lab-scale [1].

2.1. Ablative Fast Pyrolysis

BioMates processing of biomass starts with AFP. Here, the raw material is pressed in inert atmosphere against a rotating heat source at ≈ 550 °C, where it vaporises in less than 1 second. Cooling down to room temperature, the formed vapours separate into a liquid “bio-oil” and permanent gases. This bio-oil amounts to 40-70 wt % and – in the case of processing straw – 10 vol % of the feedstock.

The resulting high energy density of the bio-oil enables a cost-efficient transport (“Rail & Road” in Fig. 1), and this first processing step is preferably located in the proximity of the biomass source. This de-centralized bio-oil production will substantially contribute to strengthening rural areas. In the framework of circular economy, the use of the char (obtained as a by-product) as fertiliser to be applied onto the field it originated from, will be investigated.

Cost effectiveness of the AFP technology will be enhanced the by means of fractionated condensation and/or “in-line catalysis”, also improving the properties of the resulting bio-oil and hence facilitating its subsequent upgrading.

Here, in-line catalysis stands for subjecting the formed vapours to mesoporous or microporous materials, which are well-known means of deoxygenising pyrolysis vapours [2].

2.2. Mild Catalytic Hydrotreating

The second step, mild catalytic hydrotreating, is to be carried out preferably near the refinery that is intended to co-feed the produced intermediates. This allows for synergy effects, mainly by feeding excess hydrogen from the refinery into the mild catalytic hydrotreating plant, where it is used to turn the bio-oil into well-defined “Bio-based Intermediates” – the “BioMates”. It ensures that critical properties such as acid value, oxygen content or sulphur content are guaranteed at any time, thus enabling “BioMates” to enter the refinery processes without any need of technical consideration on the operation or final product quality.

Mild catalytic hydrotreating follows a one-step-approach that has several advantages when compared with the current state-of-the-art multiple hydroprocessing steps. The main advantage is the significant reduction of the associated H_2 consumption, which is estimated to render at least 70 % decrease of the conversion cost over the conventional approach for upgrading pyrolysis bio-oils.

Tailor-made catalyst development will be performed in order to support and optimise mild hydrotreating.

2.3. Electrochemical H_2-Processing

While the vast majority of hydrogen is circulated in continuous hydrotreating processes, the consumed amount has to be replaced by fresh H_2 – the so called *Make-up Hydrogen*. In BioMates, this stream is compressed to operation conditions by electrochemical hydrogen compression, like illustrated in Fig. 2. This single-stage isothermal process step is less energy demanding than conventional compression systems, often involving adiabatic and multi-stage piston compressors.

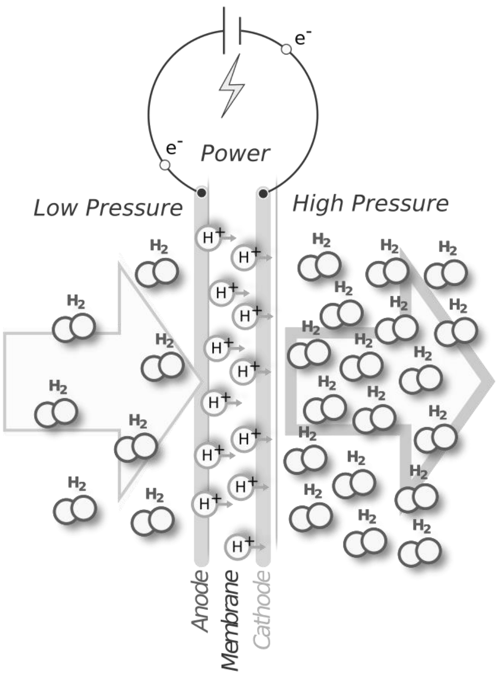

Fig. 2: The principle of electrochemical H_2-compression (figure courtesy of HyET)

2.4. Environmental, social and regulation aspects

Environmental sciences will take over a crucial part in the overall BioMates process development by interacting in feedback loops with engineering. A stakeholder workshop, scheduled for 2019, will allow interested parties from policy, industry and NGOs to become part of the BioMates process.

The issue of where to blend which bio-based material streams in or after the refinery is also a question of national and European regulation, a policy recommendation document will be developed along with the technical output of the project.

2.5. Refinery Integration

While AFP will be advantageously operated in the vicinity of feedstock production, the subsequent mild hydrotreating should be conducted within or near a refinery, enabling utilisation of excess energy and energy carriers (e.g. hydrogen). As hydrogen is the key driver of the hydroprocessing operating cost (> 95 % cost is the cost of H_2), the overall economy will be improved by lowering the costs and enhancing the sustainability of H_2 supply by envisioning refinery excess H_2 (if available).

But, of course, the key element of refinery integration is the definition of optimal insert points for BioMates within the refinery – which effects the intermediates' specifications and vice versa.

3. First results

During the first months of the project, 48 kg of bio-oil were produced from wheat straw in the TRL 4-plant, to be used for catalyst development and adjustment of mild-HDT conditions. The overall yield of the bio-oil was 21 wt % (Fig. 3).

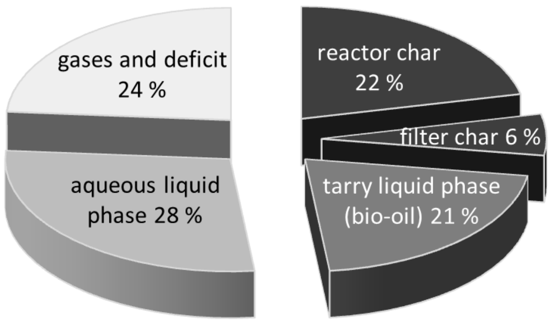

Fig. 3: Mass balance of straight-run bio-oil production from wheat straw (% = wt %)

Subjecting the bio-oil to mild catalytic hydrotreatment results in an organic phase (the BioMates) and an additional aqueous phase. Raising the temperature of mild-HDT from 200 to 380 °C at constant other parameters leads to a drastic decrease of the organic phase's acid number, like shown in Fig. 4. Along with this improvement of BioMates quality, the loss of chemical energy into the gas phase, in the figure expressed as gas-phase-concentration of CO + C1-C3-alkanes/ olefins, increases. This indicates that the operation conditions of mild-HDT will have to be optimised along with the insert points within the refinery.

Furthermore, it should be noted that while the density of the organic phase is higher than the one of the aqueous liquid phase for the low reaction temperatures, a reverse behaviour is found for the products gained at more severe reaction conditions.

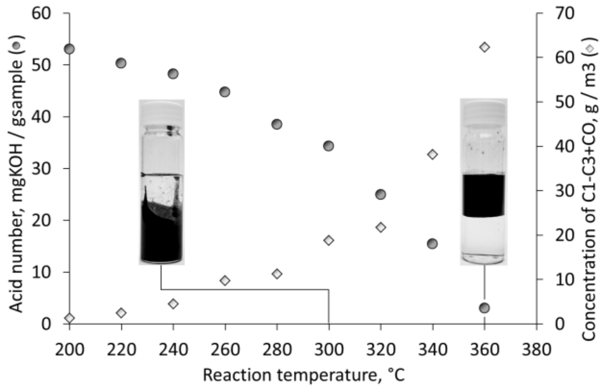

Fig. 4: Acid number of the treated bio-oil and gas-phase-concentration of CO + C1-C3-alkanes/ olefins for increasing reaction temperatures of mild-HDT. The samples indicate the dark tarry phase staying below the translucent aqueous phase for products derived at low reaction temperatures (here: 300 °C) and vice versa for products derived at higher temperatures (here: 360 °C)

4. The BioMates Project

4.1. 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 [3, 4]. 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 [5]. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 727463.

This manuscript 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.

4.2. 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*.

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