

RELIABLE BIO-BASED REFINERY INTERMEDIATES – BIOMATES

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ABSTRACT: The BioMates technology aims to convert residues and 2nd generation 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 attached to AFP as well as electrochemical H₂-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 a mixture of wheat and barley straw in a TRL 4 AFP-plant was performed with a yield of 21 wt.-% to tarry liquid product. Mild-HDT of such bio-oil lead to organic product phases with acid numbers down to 3.0 mg KOH/g for reaction temperatures of up to 360 °C.

Keywords: biofuel, fast pyrolysis, biomass to liquid, upgrading, agricultural residues

1 INTRODUCTION

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 finished fuels 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 herbaceous 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 decentralised valorisation of agricultural residues and non-food crop 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 intermediates which are deri-

ved from cellulosic biomass into conventional refineries strictly requires compatibility with the refining processes 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 attached to 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 further improves the carbon footprint and production costs of the bio-based intermediates.

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. 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].

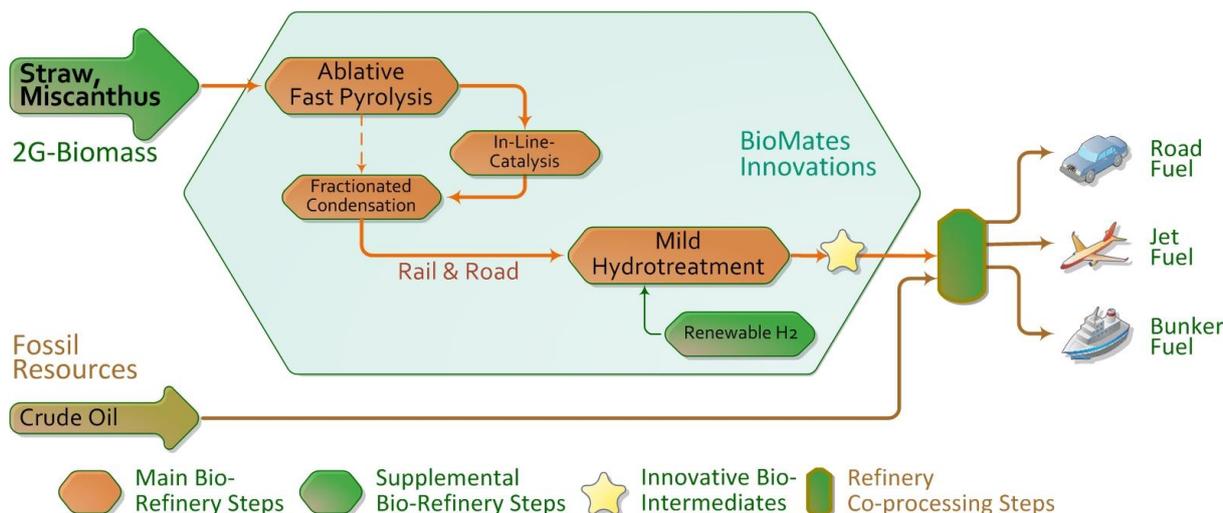


Figure 1: Schematic of the BioMates concept to produce bio-based intermediates for co-feeding in conventional refineries

2 METHODS

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 s. Cooling down to room temperature, the formed vapours separate into a liquid product and permanent gases. This liquid amounts to 40-70 wt.-% and – in the case of processing straw – 10 vol.-% of the feedstock. A more detailed description is given elsewhere [2].

The resulting high energy density of the bio-oil enables a cost-efficient transport (“Rail & Road” in Figure 1), and this first processing step is preferably located in the proximity of the biomass source in order to avoid long distance transportation of low density biomass. This decentralised 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 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 primary vapours coming from the AFP-reactor to mesoporous or microporous materials, which are well-known means of deoxygenising pyrolysis vapours [3].

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 [4, 5]. 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 to finished fuels.

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.

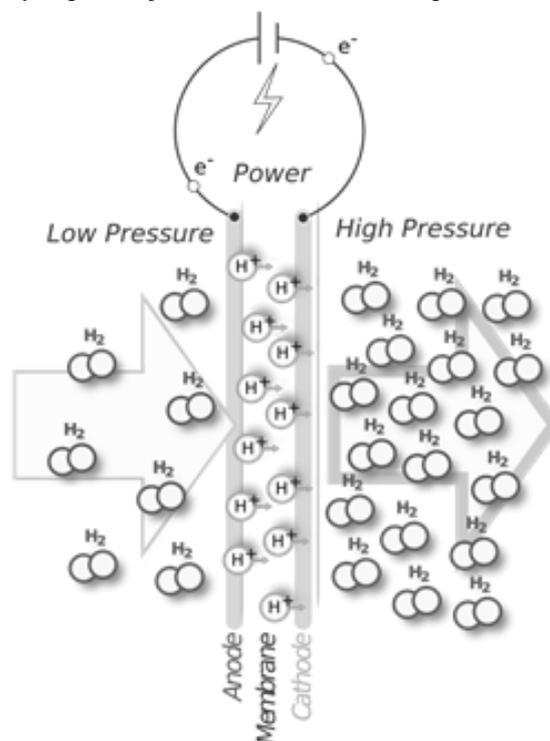


Figure 2: The principle of electrochemical H_2 -compression

This single-stage isothermal process step is less energy demanding than conventional mechanical compression systems, often involving adiabatic and multi-stage piston compressors.

Additionally, as the applied proton exchange membrane only is permeable to protons (hydrogen ions) the system can also be used for separation and purification of hydrogen overspill from the HDT reactor effluent in one step combined with repressurisation, thus avoiding the installation of a pressure swing adsorption for H₂ recovery followed by recirculation compressor.

2.4 Environmental, social and regulatory aspects

Environmental and social 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 get involved with 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 H₂), the overall economy will be improved by lowering the costs and enhancing the sustainability of H₂ supply by envisioning refinery excess H₂ (if available).

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

3 FIRST RESULTS

3.1 Ablative Fast Pyrolysis

A pilot plant at TRL4 for ablative fast pyrolysis with a nominal capacity of processing 10 kg/h briquetted biomass with a cylindrical shape (diameter of 50 mm) was used at Fraunhofer UMSICHT to produce bio-oil for first upgrading tests [2, 6-8]. The plant was used in its original setup as described above without catalytic vapour upgrade or staged condensation. The cyclone mentioned in earlier publications [6, 7] was replaced by a hot gas filter to improve the removal of fly ash and fine char particles from the vapour stream prior to condensation, although this increased the residence time of the primary vapours in a heated surrounding.

Two different herbaceous feedstocks were used: a mixture of barley/wheat straw (50 wt.-% wheat and 50 wt.-% barley straw) supplied by Erhard Meyer, Hude-Vielstedt, under the trade name "Strohfix – Gerste" and *Miscanthus x giganteus* supplied by the company Sieverdingbeck, 46342 Velen-Ramsdorf, Germany, www.sieverdingbeck-agrar.de, under the trade name "Miscanthus Häcksel Premium". Proximate and ultimate analysis of both feedstocks are given in Table I.

Table I: Proximate and ultimate analysis of biomass feedstock applied for bio-oil production

	Wheat/ barley straw	Miscanthus
Proximate analysis		
Water (wt.-%)	6.8	11.9
Ash (wt.-%, mf)	3.1	2.5
Volatiles (wt.-%, daf)	75.4	75.4
Fixed carbon (wt.-%, daf)	24.6	24.6
HHV (MJ/kg, daf)	19.3	19.4
Ultimate analysis		
C (wt.-%, daf)	49.1	50.6
H (wt.-%, daf)	5.8	4.1
N (wt.-%, daf)	0.4	-
O (wt.-%, daf) [†]	44.7	45.3
S (ppm, daf)	767	347
Cl (ppm, daf)	2,526	719
K (ppm, daf)	13,725	2,423
Ca (ppm, daf)	1,713	1,669
Mg (ppm, daf)	349	237
Na (ppm, daf)	193	16
P (ppm, daf)	-	650

mf – moisture-free basis;

daf – dry and ash-free basis

[†] calculated by difference

Table II gives an overview of the experimental conditions applied in the pilot APF plant used for the production of bio-oil.

Table II: Experimental conditions for bio-oil production

Feed material	Wheat/ barley straw	Miscanthus
Feeding rate	4.4 kg/h	4.6 kg/h
Total mass converted	270.1 kg	272.5 kg
Total experiment time (accumulated)	61.6 h	58.8 h
Pyrolysis (plate) temp.	541 °C	544 °C
Reactor (gas) temp.	442 °C	432 °C
Nitrogen input	2.5 m ³ /h (0 °C, 1,013.25 hPa)	
Hydraulic pressure	4 MPa	7 MPa
Hot vapour temp. (hot gas filter)	450 °C	
Condensation temp. (cooling bath)	4 °C	

The pyrolysis liquids from the used agricultural feedstocks undergo a phase-separation, where only the tarry phase can be used for the further main process steps within the BioMates concept. The aqueous phase is further on considered as by-product, while the tarry phase is also referred to as bio-oil.

Fig. 3 and Fig. 4 show the mass balance for both sets of experiments. Table III and Table IV give proximate and ultimate analysis of straw-based bio-oil (tarry phase) and lumped results of GS-MS/FID analysis, again for straw-based bio-oil. GC-MS/FID analysis was performed by Thuenen-Institute for Wood Research in Hamburg, Germany. The results for miscanthus-based bio-oil analysis are not yet available.

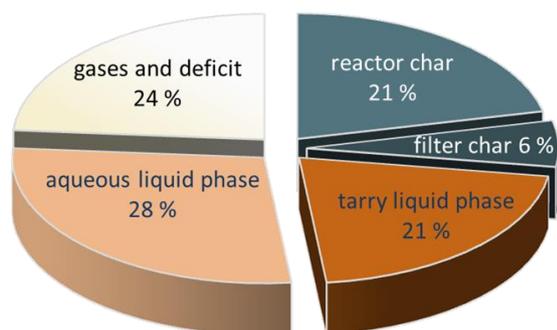


Figure 3: Mass balance: pyrolysis of straw. 100 wt.-%: biomass as received (including moisture)

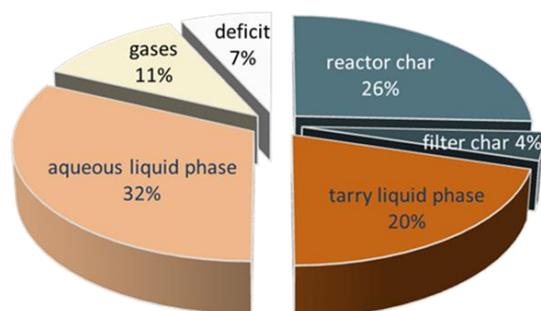


Figure 4: Mass balance: pyrolysis of miscanthus. 100 wt.-%: biomass as received (including moisture)

Table III: Analytical results of the tarry phase of the liquid products

	Wheat/ barley straw
Proximate analysis	
water (wt.%) according KF-titration	20.5
TAN (mg KOH/g) according ASTM D664	58
TAN (mg KOH/g) at buffer pH 11	185
kin. viscosity (mm ² /s, 20 °C)	725
kin. viscosity (mm ² /s, 50 °C)	55
density (g/mL, 20 °C)	1.10
HHV (MJ/kg)	23.6
Ultimate analysis	
C (wt.%)	66.7
H (wt.%)	6.7
N (wt.%)	0.8
O (wt.%) calculated by diff.	25.8
S (ppm)	553
Cl (ppm)	245

Table IV: Lumped results from GC-MS/FID analysis

	Wheat/ barley straw
based on biomass (wt.-%)	
total organics	18.2
based on condensate fraction (wt.-%)	
water	19.6
org. acids	7.3
org. alcohols	0.4
org. aldehydes	0.7
org. ketones	11.8
phenolics	19.4
sugars	3.7

First experiments with staged condensation in a side stream of the condensation part of the pilot plant were also executed for both feedstocks. Detailed results for the mixture of wheat/barley straw is given in a separate contribution to this conference [8] and preliminary results for miscanthus are published elsewhere [9]. Main findings are: as long as the vapour exit temperature from the first stage is above 65 °C for straw and 61 °C for miscanthus the resulting liquid condensate from this first stage persists as single phase liquid with lower water and acid content compared to the overall composition of liquid products from full condensation in one step (including both phases).

3.2 Mild Catalytic Hydrotreating

At University of Chemistry and Technology Prague a pilot plant for continuous bio-oil hydrotreating was used to upgrade bio-oil samples with a commercial NiMo catalyst (6.9 wt.-% Ni and 27.7 wt.-% Mo on Al₂O₃ support). The fixed bed reactor had an inner diameter of 23 mm and was electrically heated from outside. A total amount of 55 g catalyst was used for the experiment, activated with dimethyl disulphide (DMDS), to convert the transition metals to their active sulphidised form. The bio-oil applied was the tarry phase produced from wheat/barley straw mixture (see sub-section 3.1) with full condensation at 4 °C. The setpoint for the bio-oil feed pump was maintained at around 55 g/h resulting in a weight hourly space velocity of 1/h. Reaction pressure was set to 4 MPa and the hydrogen flowrate was set to 90 l/h (stp), which is approximately 8.1 g/h. The experiment was started with a reactor temperature of 200 °C and after a steady state phase the temperature was increased by 20 °C. After reaching 360 °C and a total time on stream of 90 h the reactor was shut down. More details are given elsewhere [10].

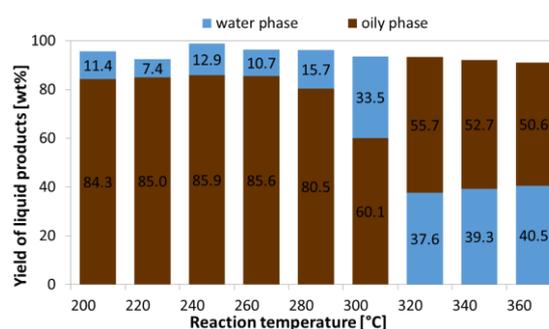


Figure 5: Yields of liquid products (oil phase and water phase) over reaction temperature

The product from hydrotreating was collected separately for the different reactor temperatures. Two phases were always observed: a clear water phase and a dark (black) oily phase. Fig. 5 shows the change in respective yields over the increasing reactor temperature. The difference to 100 % is, on one hand, solid carbon produced in the preheater and on the catalyst and, on the other hand, gaseous compounds like carbon monoxide, carbon dioxide and C₁ to C₃ hydrocarbons as methane or ethylene. For reaction temperatures from 200 °C to 260 °C no significant change in overall yields can be observed. Starting with 280 °C a steady decrease in oily phase yield and thus a steady increase in water phase yield can be observed. And between reactor temperatures of 300 °C and 320 °C a general change can also be

observed: while for temperatures below 320 °C the oily phase was below the water phase this changed for temperatures above 300 °C, where now the oily phase was on top of the water phase. This can be explained by the change in the oily phase density as depicted in Fig. 6. With increasing temperature, the resulting density of the oily phase decreases, and between 300 °C and 320 °C it passes the density of water, so at higher temperatures the density of the oily phase is lower than the one of water. Going along with the decrease in density also a considerable decrease in kinematic viscosity of the oily phase can be observed from about 215 mm²/s down to 11 mm²/s. Although the density of the oily phase always was below the density of the bio-oil fed to the hydro-treating reactor, the kinematic viscosity initially (for temperatures below 280 °C) was higher than the viscosity of the feed, which was 140 mm²/s).

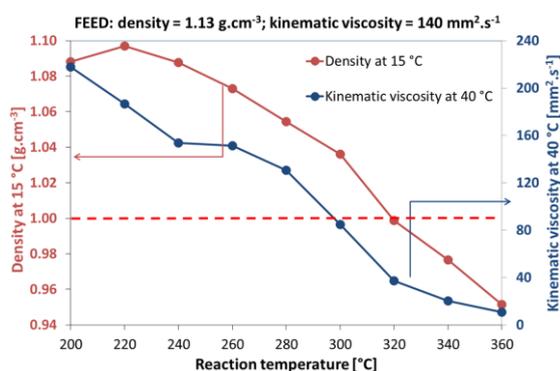


Figure 6: Density at 15 °C and kinematic viscosity at 40 °C over reaction temperature

Hydrotreatment of bio-oil is performed to reduce oxygen content and thus reduce polarity, acidity and increase miscibility with conventional hydrocarbons within refineries. Fig. 7 shows the resulting oxygen and hydrogen content of the produced upgraded oily phase as a function of reaction temperature. These values are based on the elemental analysis of the entire phase, so including the water content. With increasing reaction temperature, the oxygen content of the product was decreasing while the hydrogen content increased. In the end, at a reaction temperature of 360 °C an oxygen content below 6 wt.-% could be achieved.

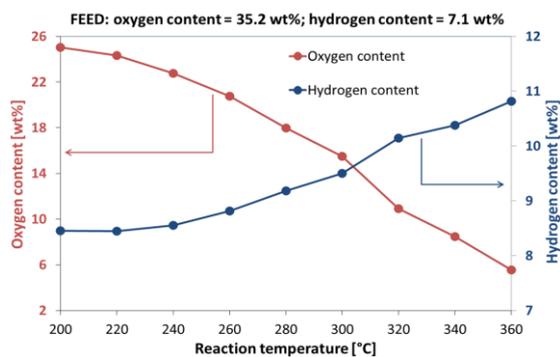


Figure 7: Oxygen and hydrogen content in oil phase over reaction temperature (hydrogen and oxygen contained in water content included)

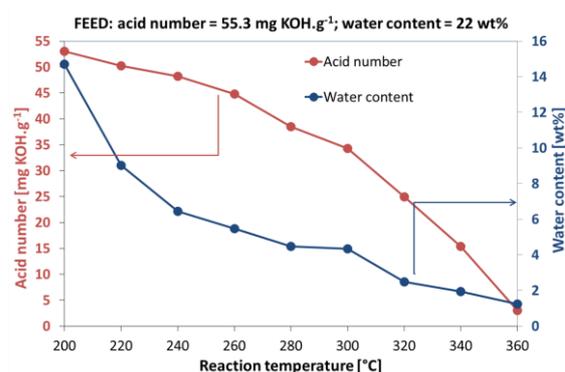


Figure 8: Acid number and water content of oil phase over reaction temperature

As can clearly be seen from Fig. 8, the decreasing oxygen content in the oily phase resulted in a decreasing acid number with increasing reaction temperature. At the highest reaction temperature, a total acid number (using a method based on ASTM D664) of 3 mg KOH/g bio-oil could be observed. Also with the decreasing oxygen content in the oily phase, the polarity of the organic matter reduced significantly and thus the ability to dissolve water dropped considerably already at low reaction temperatures. Even at 220 °C the water content of the oily phase was below 10 wt.-% and dropped further down to 1.2 wt.-% at 360 °C.

Fossil petroleum has a composition in the range of 83 wt.-% to 87 wt.-% carbon, 10 wt.-% to 14 wt.-% hydrogen and 0.1 wt.-% to 1.5 wt.-% oxygen [11]. This gives molar hydrogen-to-carbon ratios (H/C) between 1.379 and 2.024 and molar oxygen-to-carbon ratios (O/C) between 0.001 and 0.014. Table V gives elemental composition regarding carbon, hydrogen and oxygen of some of the products and for comparison reason also the values for the bio-oil fed to the hydrotreatment reactor. Here only the values for the sheer organic matter were calculated as the hydrogen and oxygen content of the oily phase caused by the dissolved water, determined with Karl-Fischer titration, was subtracted.

Table V: Elemental composition of selected products (given on dry basis; water content determined with Karl-Fischer titration subtracted)

Temperature	Feed	Product			
	-	240	280	320	360
C (wt.-%)	71.94	72.61	75.35	80.01	83.88
H (wt.-%)	7.11	8.38	9.09	10.12	10.81
O (wt.-%)	20.11	18.19	14.66	8.93	4.51
H/C	1.186	1.384	1.448	1.518	1.546
O/C	0.21	0.188	0.146	0.084	0.040

With increasing temperature and thus decreasing oxygen content, the amount of carbon and hydrogen in the organic matter increased. More important is the fact that not only the absolute hydrogen content increased with the increasing reaction temperature but also the H/C-ratio, which means that the degree of saturation increased and the H/C-ratio reached values in the lower end of petroleum. However, the O/C-ratio still is more than a factor of 4 above the typical values for petroleum, but in petroleum there is up to 6 wt.-% of sulphur, which is virtually not present in bio-oil.

4 CONCLUSIONS AND OUTLOOK

The joint project “BioMates” aims at the production of intermediate liquid energy carriers based on residual biomass from agriculture or perennial crops not competing with food/feed production. The concept considers the utilisation of classical petroleum refineries as beneficial for efficient conversion of these intermediates to finished fuels.

The principle of ablative fast pyrolysis proved to be suitable to convert herbaceous biomass like cereal straw represented by wheat and barley and perennial grasses like miscanthus into bio-char and a liquid that separates into an aqueous phase and a tarry phase. Preliminary experiments with a commercial sulphidised NiMo catalyst for hydrotreatment showed the potential of the upgrading of the tarry phase to hydrocarbon-compatible intermediates with greatly reduced oxygen and water content and also greatly reduced acid number.

The future technical work within the project will focus on improvements of the pyrolysis process as well as the hydrotreatment. In pyrolysis a staged condensation will be introduced to increase the recovery of valuable organic matter in the tarry phase and decrease the water and acid content. Additionally, a catalytic vapour treatment will be installed between the pyrolysis reactor and the condensation system to selectively remove carboxylic functional groups from the primary vapour compounds.

For the hydrotreatment step the target is to develop new catalysts that show at least similar performance like commercial ones but do not need the presence of sulphur and have a lower deactivation tendency.

The next step towards refinery integration of the intermediate products will be a miscibility study of the produced samples with several liquid streams typically present in refineries to identify most promising entry points.

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6 ACKNOWLEDGEMENTS

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

