BioMates

Deliverable D 1.1: Straight-run AFP products from straw & miscanthus

Version 01

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Contents

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.

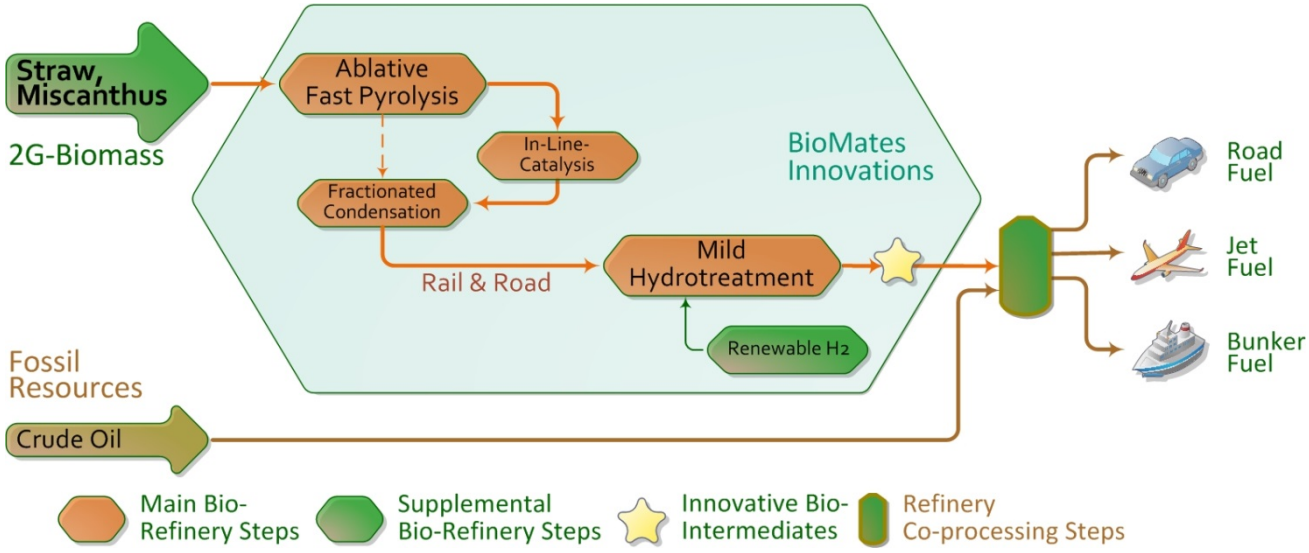

Figure 1: The BioMates-concept

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

Being of demonstrator type, deliverable D1.1 consists of 50 l of straw-based and 50 l of miscanthus-based AFP products. This accompanying report describes the operating conditions of the production of primary liquid products (especially bio-oils) and presents overall mass balances of the conversion step. Furthermore, it defines the fractions that have been sent to the partner UCTP for further upgrading.

In the production runs describes here, the AFP-plant was operated in “straight run”-mode, which means, the resulting vapours are simply cooled down in one step. A more sophisticated operation, involving in-line catalysis and/or staged condensation of the vapours, will be conducted in later project steps. First experiments have already been conducted, see section 7.4 “Staged condensation”.

3. Deliverable verification

During the straw-based-batch runs liquid products were produced amounting to 131.8 kg, which is roughly equivalent to 120 l. 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. In total 56.4 kg (51.3 l) of bio-oil as main product were produced (main stream + side-stream) from straw.

During the miscanthus-based-batch liquid products were produced amounting to 142.2 kg (129 l). In total 55.3 kg (50.3 l) of bio-oil as main product were produced (main stream + side-stream) from miscanthus.

4. Feedstock

As feedstock, 2 types of biomass were used:

- **Straw** (mixture made of barley and wheat straw - 50 wt.% each)

  Supplied by the company Erhard Meyer, 27798 Hude-Vielstedt, Germany, www.strohfix.de, under the trade name "Strohfix – Gerste".

- **Miscanthus**

  Supplied by the company Sieverdingbeck, 46342 Velen-Ramsdorf, Germany, www.sieverdingbeck-agrar.de, under the trade name "Miscanthus Häcksel Premium".

Both types of biomass were analysed; the results are given in Table 1.

Table 1: Feedstock analysis

	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) calculated by diff.	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

5. TRL 4 AFP-plant

The feed is pre-processed in a separate briquetting device into dimensionally stable briquettes, 50 mm in diameter. Afterwards, it is fed to a TRL 4 AFP-plant. In this plant, the stalk-type biomass feed is pressed onto the hot surface of a rotating disk by means of a hydraulic system with two independently operating cylinders. The pressure-controlled reactor and the feed channels are purged with nitrogen. The evolving reactor char is removed using the force of gravity. The pyrolysis vapours are cleaned from fine char in a heated hot gas filter and then fed to a condensation system. The entire hot vapour area is equipped with electrical heat tracing to prevent premature decrease below the dew point (about 280 °C). The condensation system consists of an internally cooled coil condenser and an electrostatic aerosol precipitator. The liquid

product of these two separators operated in series is collected in a joint product tank. A subsequent set of a cooler and washing drum cleans the permanent gases before they are fed to the post-combustion. A partial flow of the pyrolysis vapours can be withdrawn from the main flow and added a special treatment (hot-gas catalytic treatment, fractional condensation, etc.). A schematic of the plant is given in Figure 1.

The installed process control allows the recording of relevant process parameters (such as disk temperature, contact pressure, reactor pressure, electrical power input to the disk, condensation temperature, permanent gas quantity and main composition).

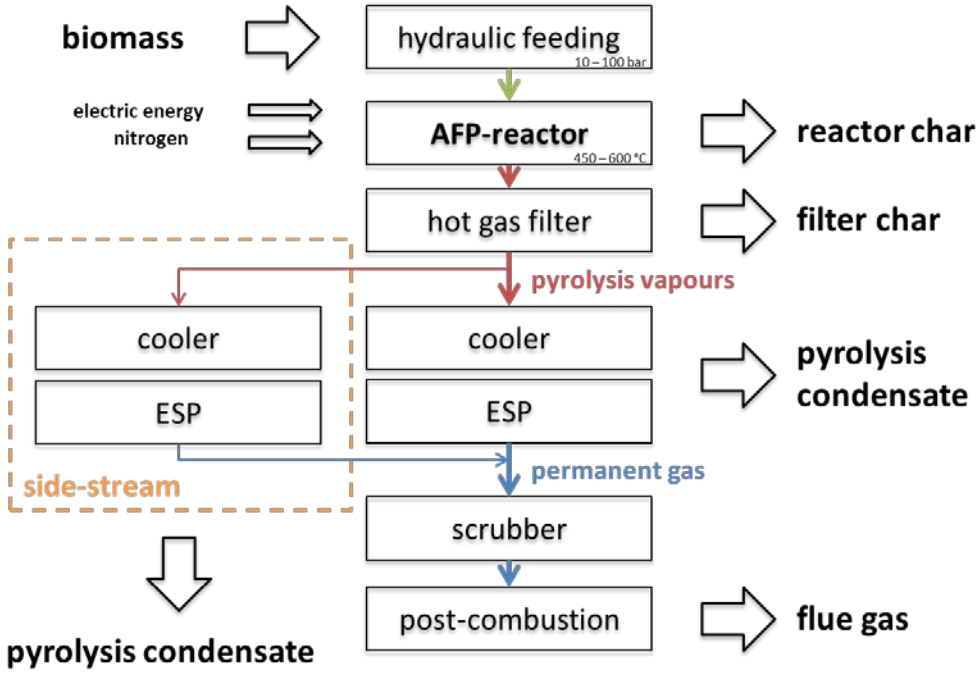

Figure 2: Structure diagram of the TRL 4 AFP-plant (ESP: electrostatic precipitator).

6. Straw-based pyrolysis products

6.1. Pyrolysis process conditions

The pyrolysis process conditions are given in Table 2.

Table 2: Pyrolysis process conditions

Feed material	wheat-/barley straw
Feeding rate	4.4 kg/h
Biomass moisture	8.6 wt.%
Total feed mass	270.1 kg
Total experiment time (sum)	61.6 h
Pyrolysis (plate) temperature	541 °C
Reactor (gas) temperature	442 °C
Nitrogen input	2.5 m^3/h (0 °C, 1,013.25 hPa)
Hydraulic pressure	4 MPa
Hot vapour temperature (hot gas filter)	450 °C
Condensation temperature (cooling bath)	4 °C

6.2. Mass balance

Solid residues were collected in 2 streams. The majority leaves the reactor by gravity as coarse char and the fines leaving the reactor together with the product vapours are separated from the gaseous stream by means of an electrically heated ceramic candle filter. The condensed liquid product immediately splits into 2 separate liquids within the catch tank: an aqueous phase floating on top of the tank and a tarry phase on the bottom. The total amount of biomass of 270.1 kg fed to the reactor led to the following amounts of products which are collected separately: 58.0 kg coarse char from the reactor, 16.0 kg fine char from the filter, 56.4 kg of tarry liquid phase (from the product catch tank and sampling system in side stream), 75.4 kg of aqueous liquid phase (from the product catch tank and sampling system in side stream) and permanent gases together with mass loss due to detection errors 64.3 kg. The relative share of each of these fractions is shown in Figure 3.

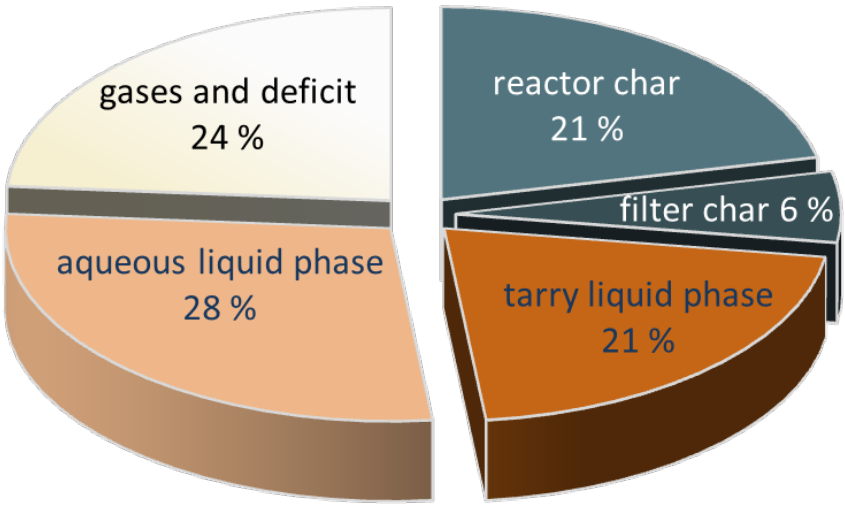

Figure 3: Mass balance: pyrolysis of straw. 100 wt.-%: biomass as received (including moisture).

6.3. Liquid product handling and shipping

The liquid product (aqueous and tarry phase) of all straw experiments was collected together in the plant's product tank. After the test series, the aqueous phase on the top was removed and the tarry phase was filled in a single canister. After one day at 4 °C, residues of the aqueous phase were removed by decanting. Afterwards the tarry phase was mixed by shaking its canister. The transport data of the straw-based tarry product phase are summarised in Table 3.

Table 3: Transport data of the straw-based tarry-phase products.

Mass tarry phase, product tank	47.9 kg
Packing	5-l-bottles
Containers shipped to UCTP	8 x 5-l-bottles
Shipping mass	44 kg (40 l)
Shipping date	27.01.2017

7. Miscanthus-based pyrolysis products

7.1. Pyrolysis process conditions

The pyrolysis process conditions are given in Table 4.

Table 4: pyrolysis process conditions

Feed material	miscanthus
Feeding rate	4.6 kg/h
Biomass moisture	13.2 wt.%
Total feed mass	272.5 kg
Total experiment time (sum)	58.8 h
Pyrolysis (plate) temperature	544 °C
Reactor (gas) temperature	432 °C
Nitrogen input	2.5 m^3/h (0 °C, 1,013.25 hPa)
Hydraulic pressure	7 MPa
Hot vapour temperature (hot gas filter)	450 °C
Condensation temperature (cooling bath)	4 °C

7.2. Mass balance

In addition to the procedure described in section 6.2, the permanent gases' mass was detected explicitly for each production run.

In total, 272.5 kg of miscanthus (236.3 kg dry mass) were processed into 55.3 kg of tarry liquid product, 87.0 kg of aqueous liquid product, and 30.6 kg of gases. 70.0 kg of coarse char were collected from the reactor and 10.8 kg of fine char from the filter. The deficit of the mass balance is 18.7 kg. The relative shares are presented in Figure 4.

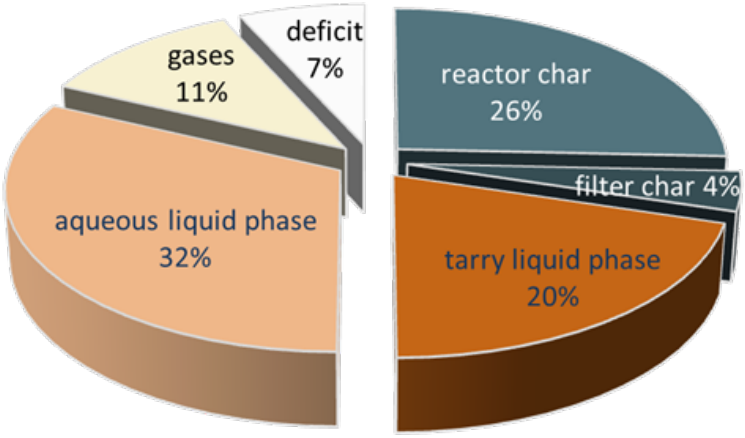

Figure 4: Mass balance: pyrolysis of miscanthus. 100 wt.-%: biomass as received (including moisture).

Most of the tarry liquid phase accrued as total condensate, but some shares were derived as fractions of staged condensation in the side-stream (see Table 5 and section 7.4). In Figure 4, they are all summed up as "tarry liquid phase".

7.3. Liquid product handling and shipping

The post-treatment of the liquid product was performed according to the routine for straw-based products like described in section 6.3, with the exception that the tarry phase now was mixed by means of a stirrer. The relevant transport data are summarised in Table 5.

Table 5: Transport data of the miscanthus-based tarry-phase products

Mass tarry phase, product tank	51.0 kg
Packing	5-l-bottles, 1-l-bottles
Containers shipped to UCTP	8 x 5-l-bottles (tarry phase – total condensate) 5 x 1-l-bottles (staged condensate)
Shipping mass tarry phase total condensate	42.4 kg
Shipping mass staged condensate (100 °C)	0.84 kg
Shipping mass staged condensate (80 °C)	0.82 kg
Shipping mass staged condensate (70 °C)	0.99 kg
Shipping mass staged condensate (60 °C)	1.11 kg
Shipping mass staged condensate (40 °C)	0.83 kg
Total shipping mass	47.0 kg
Shipping date	16.05.2017

7.4. Staged condensation

Staged condensation experiments (two cascading staged-condensation-chains, consisting of a cooler and an electrostatic precipitator (ESP) each) were installed and operated in the side-stream. The vapour condensate and the precipitated aerosol from each stage (1st and 2nd stage) were collected together in a cooled flask. The condensation temperature of the 1st stage (cooler and ESP) was varied by adjusting the cooling-medium temperature to 60 °C, 65 °C, 70 °C and 80 °C. The temperature of the 2nd stage (cooler and ESP) was kept constant at 4 °C. The vapour temperatures reported further on were measured by using PT 100 temperature sensors in the gas stream after the ESP of each stage.

For each condensation temperature, the masses of water and organics in the tarry (and, if applicable, in the aqueous) phase of the 1st stage were determined. The results are compared to the mases of the 2nd stage-condensates in Figure 5.

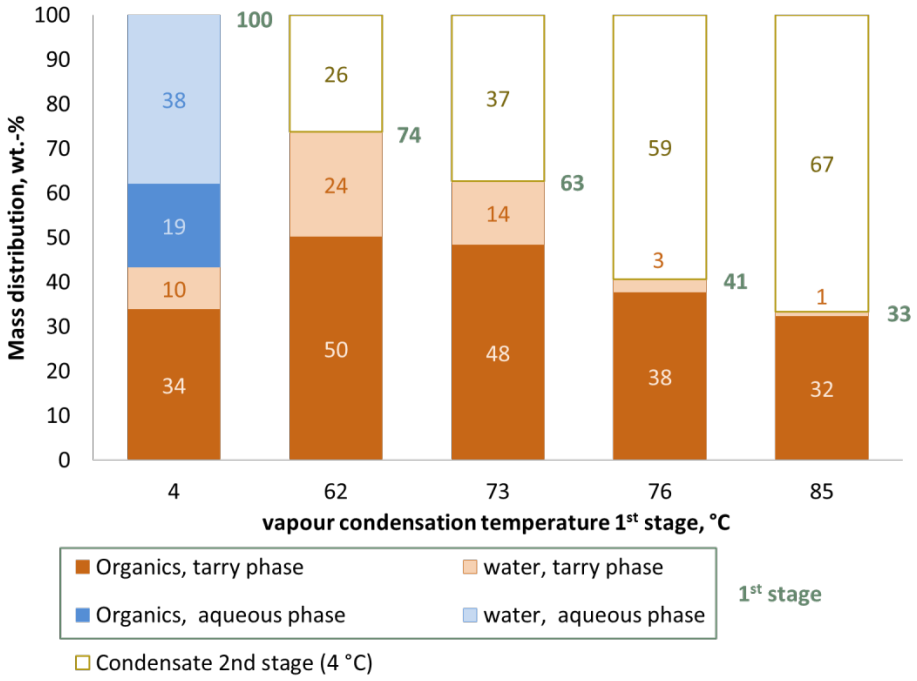

Figure 5: Staged condensation of miscanthus in the side-stream.
(The deviations for 4 and 73 °C between the single-component-percentages' sum and the overall respectively 1st-stage-percentages are due to rounding errors.)

8. Analytics of selected products

The results of analytics of the main products, as far as available yet, are listed in Table 6 (tarry liquid products) and Table 7 (char).

Table 6: Analytical results of the tarry phase of the liquid products (as far as available)

	Wheat / barley straw	Miscanthus
Proximate analysis		Not available yet
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 7: Results of product-char analysis (reactor- and filter-char)

	Wheat / barley straw	Miscanthus
Proximate analysis		
Water (wt.%)	1.7	1.3
Ash (wt.%, mf[#])	11.0	7.3
Volatiles (wt.%, daf*)	33.1	46.4
Fixed carbon (wt.%, daf)	66.9	53.6
HHV (MJ/kg, daf)	30.2	27.2
Ultimate analysis		
C (wt.%, daf)	77.2	70.0
H (wt.%, daf)	4.4	4.8
N (wt.%, daf)	0.8	0.3
O (wt.%, daf) calculated by diff.	17.6	24.9
S (ppm, daf)	1,664	583
Cl (ppm, daf)	6,931	828
K (ppm, daf)	46,887	7,545
Ca (ppm, daf)	6,802	4,501
Mg (ppm, daf)	1,306	868
Na (ppm, daf)	727	73
P (ppm, daf)	2,699	1,708

[#]mf – moisture-free basis;
*daf – dry and ash-free basis

9. 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.

10.Literature

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