# **BioMates**



Deliverable D 1.2: Advanced-AFP products from straw & miscanthus

Version 02

Grant Agreement number:	727463
Project Acronym:	BioMates
Project title:	Reliable Bio-based Refinery Intermediates — BioMates
Start date of the project:	01.10.2016
Duration of the project:	30.09.2020
Deliverable N°.:	D06
Relative Deliverable N°.:	D1.2
Work Package N°. Task N°.:	WP1, Task 2
Deliverable title	Advanced AFP products from straw & miscanthus
Scheduled date of submission	30/09/2017
Date of submission of Version 01:	29/09/2017
Version:	02
Date of submission of this version:	30/05/2018
Dissemination Level:	Public
Project website address:	www.biomates.eu
The deliverable is elaborated on the basis of	the original Grant Agreement
Submitting party:	Fraunhofer
Responsible author:	Stefan Conrad
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Reviewer:	
Verification:	2 x 50 l of advanced-AFP products

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





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# **1. Introducing BioMates**

### 1.1. The BioMates Project

The BioMates project aspires in combining innovative 2<sup>nd</sup> generation biomass conversion technologies for the cost-effective production of *bio*-based inter*m*edia*tes* (BioMates) that can be further upgraded in existing oil refineries as renewable and reliable co-feedstock. 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<sub>2</sub>-compression** and the state-of-the-art **renewable H<sub>2</sub>-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 2<sup>nd</sup> 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

BioMates processing of biomass starts with AFP. Here, the raw material is pressed in inert atmosphere against a rotating heat source at about 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. The resulting high energy density of the bio-oil enables a cost-efficient transport ("Rail & Road" in Figure 1). This is supposed to enable decentralized bio-oil production that will substantially contribute to strengthening rural areas.

During the first years of the BioMates project, a TRL 4 AFP-plant is operated to fine-tune the pyrolysis procedure and to produce first batches of samples for subsequent mild-HDT and hydrotreatment catalyst development.

At the very beginning, the TRL 4 AFP-plant had been used in "straight-run mode", where the resulting vapours were simply cooled down and fractionated in a one-step-condensation. For wheat straw, this production (with subsequent phase separation) yielded 21 wt.-% of tarry liquid product phase (the bio-oil) /Heil-2017/.

During test runs (performed within Task 1.1 of the project), the verification of two improving technologies already had been performed in a side-stream: *ex-situ in-line catalysis* and *fractionated condensation*. Here, in-line catalysis stands for subjecting the formed vapours to mesoporous or microporous materials, which are well-known means of deoxygenising pyrolysis vapours /Aho-2010/.

Afterwards, the TRL 4 AFP-plant has been upgraded in order to allow improving technologies in the main product stream, too. The completion of this part of the work marked the milestone MS3. The upgrading covered the design, purchase and integration

- of a fixed bed reactor for ex-situ in-line catalysis and
- a two-stage condensation train in the main stream.



With this upgraded plant, 50 l-batches of both straw-based and miscanthus-based bio-oils have been produced, which is the subject of the deliverable report at hand.

## 3. Deliverable verification

The verification of D 1.2, production of upgraded bio-oil from both feedstock materials, straw and miscanthus, could not start before the achievement of milestone MS3, which was completed with 2  $\frac{1}{2}$  months delay on 24/10/17.

Meanwhile (and in addition to the original production plan) 70 l straw-based straight-run bio-oil (tarry phase) were produced for further mild-HDT catalyst tests in WP 2. Anyhow, the development of operating conditions, especially for staged condensation, was already started as "side-effect" of Task 1.1, like stated above.

In particular, the *production of upgraded bio-oil* by ex-situ in-line catalytic vapour upgrade was tested using 6 different catalysts in side stream operation of the fixed bed reactor. For these tests only straw was used as feedstock. The results show that the composition and hence the properties/quality greatly varies with time on stream and a single, fixed bed reactor is no suitable solution. Based on the results a staged condensation without a fixed bed catalytic reactor was the best option producing the advanced bio-oils. Although, full stream experiments with the two best-performing catalysts will be conducted later on to get full mass and energy balance for this approach.

Processing mixed wheat/barley-straw, advanced bio-oils (single-phase liquid from the 1<sup>st</sup> condensation stage) were produced amounting 76.2 kg. An amount of 56 kg was shipped to CERTH and an amount of 6.7 kg was shipped to UCTP on 25/01/2018 with a delay of 3 ½ months.

Producing the miscanthus-based batch led to 80.2 kg of advanced bio-oils (single-phase liquid from the 1<sup>st</sup> condensation stage). An amount of 68.6 kg was shipped to CERTH and an amount of 6.1 kg was shipped to UCTP on 04/04/2018 with a delay of 6 months.

## 4. Upgraded TRL 4 AFP-plant

In the upgraded TRL 4 AFP-plant, pyrolysis vapours produced in the ablative reactor are cleaned from fine char particles in a hot gas filter. Downstream of the hot gas filter, an ex-situ catalytic fixed bed reactor can be optionally installed. The upgrading process is done in the vapour phase by passing the reactor filled with catalyst pellets from top to bottom at an adjustable temperature between 300 °C and 600 °C. The upgraded vapours are condensed in two stages. The first stage was installed additionally in the course of Task 1.2 and consists out of an internally and jacket-cooled condenser and a jacket-heated electrostatic aerosol precipitator operated at the same temperature as the preceding condenser. The vapour condensates and precipitated aerosols are collected separately in two non-tempered vessels. Both single-phase tarry-like fractions (vapour condensate and precipitated aerosols) will be merged after each experiment. This first stage condensation step can be operated at temperatures between 20 °C to 120 °C. Results from Deliverable D 1.1 have shown that condensation temperatures between 60 °C and 80 °C produce single-phase condensate fractions with optimised organic, decreased water and acid contents. The initial total condensation unit, which consists out of an intensive cooler and an electrostatic precipitator, is further used as 2<sup>nd</sup> condensation step. The aqueous 2<sup>nd</sup> stage vapour condensate and captured aerosols are collected together in a product tank. A basis sketch of the upgraded TRL 4 AFP-plant is given in Figure 2.



Figure 2: Upgraded TRL 4 AFP-plant system<sup>1</sup>

The whole system can be operated optional with and without the catalytic reactor. Temporarily, differentiated condensate samples can be taken bevor and after each additional process step (catalytic reactor and 1<sup>st</sup> condensation step). Figure 3 shows drawings of the catalytic reactor and Figure 4 the 1<sup>st</sup> stage condensation step.





Figure 4: 1<sup>st</sup> stage condensation step (condenser on the right and ESP<sup>1</sup> on the left side)

Figure 3: Ex-situ inline catalysis reactor



The upgraded AFP-plant is also described in more detail in the report to MS3. As this report is confidential, three publishable pictures are again included here: the in-line-catalysis reactor - here operated in the side-stream – is shown in Figure 5, the first condensation stage of the main stream (before insulation and during operation) in Figure 6 and Figure 7.



Figure 5: The in-line-catalysis reactor (the clearly visible, insulated device) - here operated in the side-stream



Figure 6: The first condensation stage of the main stream (the clearly visible part), consisting of cooler (right column) and electrostatic precipitator (left column), before...



Figure 7: ...and after insulation



After some preliminary experiments, the bio-oil production on the upgraded TRL4 AFP-plant started on 27/11/2017 with the straw-based batch. On 06/02/2018, the feedstock was switch to miscanthus.

## 5. Upgraded TRL 4 AFP products in the side-stream

## 5.1. Preliminary verification of fractionated condensation

Both straw-based and miscanthus-based bio-oils decompose into two distinct phases. Compared to the tarry phase of the total bio-oil (4 °C), staged condensates with a similar water content showed more usable organics in the target fraction. Furthermore, it was demonstrated that the quantity and quality (water content and TAN) of usable organic fractions can be significantly increased by condensing the vapours in stages. The minimum vapour temperature at which the 1<sup>st</sup> stage condensates will be a single-phase bio-oil was found to be 66 °C for wheat/barley straw (see Figure 8) and 62 °C for miscanthus (see Figure 9).

Additionally, the valuable components from the aqueous phase will be found in the first condensate fraction (long-chained molecules), while a part of the undesirable compounds (like acids) will be found in the  $2^{nd}$  stage. Aiming at a high yield of usable organics in single-phase liquids and at an as-low-as-possible water and acid content, a condensation temperature range of 60 °C – 80 °C was determined to be adequate for both feedstocks.





<sup>&</sup>lt;sup>2</sup> Deviations of the single numbers' sums from 100 % for the whole column or from the 1<sup>st</sup>-stage-sum are due to rounding errors. Version 02, 30/05/2018







#### 5.2. Preliminary verification of ex-situ in-line catalysis

The catalytic reactor originally designed for use in the main stream was also used for preliminary tests in the side-stream. For this test with lesser vapour streams (about 5 wt.-% of the produced total vapours), the amount of catalyst was only a thin layer within the reactor and the remaining unused "dead volume" of the reactor was filled with glass beads. The temperature inside the reactor was measured at the catalyst bed. The upgraded vapours were condensed in a single step by using a coil condenser and an electrostatic aerosol precipitator. For producing a reference sample, the total reactor volume was filled with glass beads for minimizing effects for different vapour residence times. Different activated-carbon-catalyst, aluminium oxide and zeolite catalysts were tested at different temperatures and vapour-to-catalyst-ratios. For each tested catalyst and operating temperature a set of condensate samples is taken during a period of several hours over some experimental days. Each single-sample was collected during about 90 min. The hole testing time had to be split into several experiments. One experiment consists out of 1-3 samples. The mass and analytic parameters for each experiment were calculated based on the associated samples.

Six catalysts were tested. These are two activated carbons (product names SC40 and SC44), γ-Al<sub>2</sub>O<sub>3</sub>, zeolite (HZSM-5), zeolite modified with 5 wt.-% Ni (HZSM-5/5%Ni) and 10 wt.-% Ni (HZSM-5/10%Ni). SC40 and SC44 were commercially available from Silcarbon Aktivkohle GmbH (Kirchhundem, Germany). The γ-Al<sub>2</sub>O<sub>3</sub> catalyst was purchased from Thermo Fisher (Kandel) GmbH (Karlsruhe, Germany). The zeolite catalyst, HZSM-5, was purchased from ACS Material LLC (Pasadena, USA). Two modified zeolite catalysts, HZSM-5/5%Ni and HZSM-5/10%Ni, were modified respectively with 5 wt.-% and 10 wt.-% of nickel ions by our project partner Ranido sro (Prague, Czech Republic). According to different standard methods, a variety of properties were analysed, including water content, total acid number (TAN), higher heating value (HHV), elemental composition (C, H, O, etc.), and chemical composition (acids, alcohols, aldehydes, etc.). The analytical results



from the 1<sup>st</sup> experiment for each catalyst are given in Table 1 based on bio-oil (sum of tarry and aqueous phase) and in Table 2 based on tarry phase.

	RS	AC 1	AC 2	γ-Al2O3	HZSM5	HZSM5/5%Ni	HZSM5/10%Ni
Organics (wt%)	49.5	27.1	44.4	46.1	48.9	47.3	47.8
C (wt%)	30.5	15.1	25.8	26.8	28.4	28.5	30.0
H (wt%)	8.1	10.3	9.7	8.8	8.8	8.9	9.9
N (wt%)	0.5	0.3	0.4	0.5	0.4	0.4	0.5
O <sup>1</sup> (wt%)	60.9	74.3	64.1	63.9	62.4	62.2	59.6
S (wt%)	0.03	0.01	0.02	0.02	0.03	0.02	0.03
Cl (wt%)	0.02	0.02	0.01	0.02	0.03	0.03	0.03
TAN (mg KOH/g)	71.4	74.7	85.1	81.4	86.5	70.0	64.5
HHV (MJ/kg)	12.8	6.0	10.9	10.4	11.3	12.3	12.7

Table 1: Average values (based on the total bio-oils) performed with different catalyst at 400 °C

RS – Reference sample; AC – activated carbon

 $^{1}$ O (wt.%) = 100 (wt.%) – C (wt.%) – H (wt.%) – N (wt.%)

Table 2: Average values (based on tarry phase) performed with different catalyst at 400 °C

	RS	AC 1	AC 2	γ-Al2O3	HZSM5	HZSM5/5%Ni	HZSM5/10%Ni
Organics (wt%)	83.7	93.1	76.7	84.1	82.1	82.1	83.7
C (wt%)	57.6	67.8	49.8	56.4	55.3	55.3	58.2
H (wt%)	7.6	8.7	8.7	8.1	8.4	8.0	8.0
N (wt%)	0.7	0.7	0.7	0.7	0.7	0.6	0.8
O <sup>1</sup> (wt%)	34.1	22.8	40.8	34.8	35.6	36.1	33.0
S (wt%)	0.05	0.02	0.04	0.04	0.05	0.04	0.05
Cl (wt%)	0.02	0.01	0.01	0.02	0.02	0.02	0.02
TAN (mg KOH/g)	66.7	49.6	81.1	92.0	98.8	62.6	57.2
HHV (MJ/kg)	24.2	29.6	20.5	23.2	23.0	24.3	24.5
GC-MS/FID (wt%)							
Acids <sup>2</sup>	4.8	3.6	5.4	5.0	5.0	5.1	4.9
Ketones <sup>3</sup>	3.2	0.3	3.4	3.0	3.4	3.1	2.9
Furans <sup>4</sup>	1.2	0.1	0.8	0.6	1.0	1.0	1.0
Phenols <sup>5</sup>	1.0	3.7	1.4	1.3	1.2	1.2	1.3
Guaiacols <sup>6</sup>	2.6	3.5	2.9	2.8	3.1	3.0	3.1
Syringols <sup>7</sup>	1.1	0.9	1.2	1.2	1.3	1.2	1.2
Levoglucosan	0.8	0.4	0.5	0.4	0.5	0.6	0.6

RS – Reference sample; AC – activated carbon

 $^{1}$ O (wt.-%) = 100 (wt.-%) – C (wt.-%) – H (wt.-%) – N (wt.-%)

<sup>2</sup> Acetic acid; Propionic acid

<sup>3</sup> 1-Hydroxy-2-propanone; 1-Hydroxybutan-2-one; 2-Cyclopenten-1-one; 2-Hydroxy-3-methyl-2-cyclopenten-1-one

<sup>4</sup> 2-Furaldehyde; 2-Furanmethanol; 2(5H)-Furanone

<sup>5</sup> Phenol; 4-Ethylphenol

<sup>6</sup> 2-Methoxyphenol; 4-Ethyl-2-methoxyphenol; Isoeugenol trans; Vanillin

<sup>7</sup> 2,6-Dimethoxyphenol; 4-Ethyl-2,6-dimethoxyphenol

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Over all tests, the use of catalysts led to a decrease of organics based on the produced bio-oil, especially by activated carbons. From the tested catalysts, HZSM-5 showed the highest organic content. Among all used catalysts, zeolite catalysts showed the best performance, resulting in the bio-oils with the highest content of organics (47-49 wt.-%), carbon (28-30 wt.-%), HHV (11-13 MJ/kg) and lowest oxygen content (60-62 wt.-%). No significant improvement in comparison to the reference sample could be observed. The activated carbon catalysts showed a drastic reduction in the amount of organics. AC 1 was the most efficient catalyst, resulting in changing the quality (regarding target tarry phase) of the bio-oil (see Table 2). However, the extremely low amount of organics based on the bio-oil make them highly economically unattractive. In summary, the quality could not be increased by the tested catalysts, catalytic process conditions and fixed bed application. Furthermore, the quantity of organics (see Figure 10) and other properties varies with time on stream and a single, fixed bed reactor is no suitable solution.

In further work, the quantity of the catalytically upgraded target bio-oil has to be investigated. For this purpose, further tests in the main stream are planned to get a complete mass balance for the two catalysts showing the highest activity: SC40 and HZSM-5/10%Ni.







# 6. Upgraded AFP products in the main-stream

## 6.1. Straw-based pyrolysis products

#### 6.1.1. Pyrolysis process conditions

The pyrolysis process conditions are given in Table 3.

Table 3: pyrolysis process conditions

Feed material	wheat-/barley straw
Feeding rate	5.2 kg/h
Biomass moisture	8.6 wt%
Total feed mass	327.2 kg
Total experiment time (sum)	63.5 h
Pyrolysis (plate) temperature	550 °C
Reactor (gas) temperature	442 °C
Nitrogen input	2.5 m³/h (0 °C, 1,013.25 hPa)
Hydraulic pressure	4 MPa
Condensation temperature 1 <sup>st</sup> stage (cooling bath)	76 °C
Condensation temperature 1 <sup>st</sup> stage (vapours)	74.6 °C
Condensation temperature 2 <sup>st</sup> stage (cooling bath)	4 °C
Condensation temperature 2 <sup>st</sup> stage (vapours)	9 °C

#### 6.1.2. Mass balance

In total, 327.2 kg of wheat-/barley straw (299.1 kg dry mass) were processed into 76.2 kg of 1<sup>st</sup> stage liquid product, 83.8 kg of 2<sup>nd</sup> stage liquid product, and 70.0 kg of gases. 77.9 kg of coarse char were collected from the reactor and 13.4 kg of fine char from the filter. The deficit of the mass balance is 5.9 kg. The relative shares are presented in Figure 11.







Based on the biomass input, 23 wt.-% of 1<sup>st</sup> stage target liquid product could be produced with a water content of 19.7 wt.-%. About 26 wt.-% of the original biomass were collected as organics in the total liquid products in the used pyrolysis system using wheat-/barley straw as feedstock. 19 wt.-% of the original biomass were found as organic compounds in the 1<sup>st</sup> staged target liquid product. As expected from the preliminary verification in the side-stream experiments the organic yield in the target product could be increased compared to one-step condensation (17 wt.-% of the original biomass as organic compounds in the used tarry phase, see deliverable D1.1).

#### 6.1.3. Liquid product handling and shipping

The post-treatment of the liquid product was performed according to the routine. The liquids from the 1<sup>st</sup> stage condenser and the liquids from the 1<sup>st</sup> stage ESP were merged after the experiment and mixed by means of a stirrer. The relevant transport data are summarised in Table 4.

Mass 1 <sup>st</sup> stage condensate, product tank	76.2 kg
Packing	5-l-bottles, 1-l-bottles
Containers shipped to CERTH	10 x 5-l-bottles (1 <sup>st</sup> stage condensate) 56.0 kg
Containers shipped to UCTP	1 x 5-l-bottles (1 <sup>st</sup> stage condensate) 5.6 kg
	1 x 1-l-bottle (1 <sup>st</sup> stage condensate) 1.1 kg
Total shipping mass	62.7 kg
Shipping date	25.01.2018

Table 4: Transport data of the straw-based upgraded liquid products

#### 6.2. Miscanthus-based pyrolysis products

#### 6.2.1. Pyrolysis process conditions

The pyrolysis process conditions are given in Table 5.

 Table 5:
 pyrolysis process conditions

Feed material	miscanthus
Feeding rate	4.6 kg/h
Biomass moisture	13.3 wt%
Total feed mass	258.0 kg
Total experiment time (sum)	55.8 h
Pyrolysis (plate) temperature	548 °C
Reactor (gas) temperature	425 °C
Nitrogen input	2.5 m³/h (0 °C, 1,013.25 hPa)
Hydraulic pressure	7 MPa
Condensation temperature 1 <sup>st</sup> stage (cooling bath)	75 °C
Condensation temperature 1 <sup>st</sup> stage (vapours)	73.2 °C
Condensation temperature 2 <sup>st</sup> stage (cooling bath)	4 °C
Condensation temperature 2 <sup>st</sup> stage (vapours)	9 °C



#### 6.2.2. Mass balance

In total, 258.0 kg of miscanthus (223.6 kg dry mass) were processed into 80.2 kg of 1<sup>st</sup> stage liquid product, 61.2 kg of 2<sup>nd</sup> stage liquid product, and 41.6 kg of gases. 55.2 kg of coarse char were collected from the reactor and 13.7 kg of fine char from the filter. The deficit of the mass balance is 6.0 kg. The relative shares are in Figure 12.



Figure 12: Mass balance: pyrolysis of miscanthus including staged condensation. 100 wt.-%: biomass as received (including moisture).

Based on the biomass input, 31 wt.-% of 1<sup>st</sup> stage target liquid product could be produced with a water content of 20.7 wt.-%. About 31 wt.-% of the original biomass were collected as organics in the total liquid product in the used pyrolysis system using miscanthus as feedstock. 25 wt.-% of the original biomass were found as organic compounds in the 1<sup>st</sup> staged target liquid product. Compared to one-step condensation the organic yield could be increased significantly (16 wt.-% of the original biomass as organic compounds in the used tarry phase, see deliverable D1.1). A reason for the bigger increase is that the aqueous phase (single stage condensation) from miscanthus retains more organics compared to straw-based bio-oil. These organics can be combined in the 1<sup>st</sup> stage condensate.

## 6.2.3. Liquid product handling and shipping

The post-treatment of the liquid product was performed according to the routine. The liquids from the 1<sup>st</sup> stage condenser and the liquids from the 1<sup>st</sup> stage ESP were merged after the experiment and mixed by means of a stirrer. The relevant transport data are summarised in Table 6.

Mass 1 <sup>st</sup> stage condensate, product tank	80.2 kg
Packing	5-l-bottles
Containers shipped to CERTH	12 x 5-I-bottles (1 <sup>st</sup> stage condensate) 68.6 kg
Containers shipped to UCTP	1 x 5-l-bottle (1 <sup>st</sup> stage condensate) 6.1 kg
Total shipping mass	74.7 kg
Shipping date	04.04.2018

 Table 6: Transport data of the miscanthus-based upgraded liquid products



## 6.3. Analytical results

The results of analytics of the main liquid products, as far as available yet, are listed in Table 7 (advanced-AFP liquid products).

	wheat / barley straw	miscanthus
Proximate analysis		
water (wt%) according KF-titration	19.7	20.7
CAN (mg KOH/g) according ASTM D664	Not available yet	Not available yet
TAN (mg KOH/g) according ASTM D664	Not available yet	Not available yet
kin. viscosity (mm²/s, 20 °C)	Not available yet	Not available yet
density (g/mL, 20 °C)	1.1	1.2
HHV (MJ/kg)	22.3	20.3
Solids (wt.%) according ASTM D7579 <sup>1</sup>	0.4	0.9
Ultimate analysis		
C (wt%)	51.2	48.3
H (wt%)	7.9	7.3
N (wt%)	0.8	0.2
O <sup>2</sup> (wt%) calculated by diff.	40.1	43.6
S (ppm)	450	200
Cl (ppm)	240	340
GC-MS/FID (wt%)		
Acids <sup>3</sup>	7.0	Not available yet
Ethylene glycol	0.8	Not available yet
Ketones <sup>4</sup>	4.2	Not available yet
Furans <sup>5</sup>	0.5	Not available yet
Phenols <sup>6</sup>	0.8	Not available yet
Guaiacols <sup>7</sup>	2.1	Not available yet
Syringols <sup>8</sup>	1.0	Not available yet
Levoglucosan	1.2	Not available yet

Table 7: Analytical results of the advanced liquid products (as far as available)

<sup>1</sup> solvent: methanol/dichlormethane 1:1

<sup>2</sup>O (wt.%) = 100 (wt.-%) – C (wt.-%) – H (wt.-%) – N (wt.-%)

<sup>3</sup> Acetic acid; Propionic acid

<sup>4</sup> 1-Hydroxy-2-propanone; 1-Hydroxybutan-2-one; 2-Hydroxy-3-methyl-2-cyclopenten-1-one

<sup>5</sup> 2-Furanmethanol; 2(5H)-Furanone

<sup>6</sup> Phenol; 4-Ethylphenol

<sup>7</sup> 2-Methoxyphenol; 4-Ethyl-2-methoxyphenol; Isoeugenol trans; Vanillin

<sup>8</sup> 2,6-Dimethoxyphenol; 4-Ethyl-2,6-dimethoxyphenol



## 7. 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.

### 8. Literature

- Aho-2010 Aho, A. et al., *Catalytic deoxygenation of cellulose pyrolysis vapours over mesoporous materials*, Cellulose Chemistry and Technol. 44 (2010), 89–96.
- 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, 22.1.2014, 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, 22.1.2014,http://eurlex.europa.eu/resource.html?uri=cellar:1bd46c9o-bdd4-11e4-bbe1o1aa75ed71a1.0001.03/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*
- Heil, Volker; Schulzke, Tim; Bezergianni, Stella; Kubička, David; Fuels from Reliable Bio-based Refinery Intermediates – BioMates; Proceedings of the 11<sup>th</sup> International Colloquium Fuels - Conventional and Future Energy for Automobiles, June 27-29, 2017, Esslingen / Germany, DOI: 10.24406/UMSICHT-N-487569