BioMates

Report on analytics of feedstocks, in-line catalysts and AFP bio-oils

Version 01

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°.:	D19
Relative Deliverable N°.:	D1.4
Work Package N°. Task N°.:	WP1, Task 2
Deliverable title:	Report on analytics of feedstocks, in-line catalysts and AFP bio-oils
Scheduled date of submission	30/06/2018
Date of submission of Version 01:	11/10/2018
Version:	01
Date of submission of this version:	11/10/2018
Dissemination Level:	Public
Project website address:	www.biomates.eu
The deliverable is elaborated on the basis of	the original Grant Agreement
Submitting party:	Fraunhofer
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Reviewer:	-
Verification:	Report with summary

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

Summary

Feedstock, products (bio-oils, char) and inline-catalysts for Ablative Fast Pyrolysis (AFP), used and derived within Work Package 1 of the BioMates project, were analysed. Orbitrap mass spectroscopy, ultimate analysis and various methods of proximate analysis were applied to the feedstock as well as to the solid and liquid products. In-line catalysts (activated carbons and alumina as well as both impregnated and unimpregnated zeolites) were characterised by nitrogen physisorption.

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*mediates* (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_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.

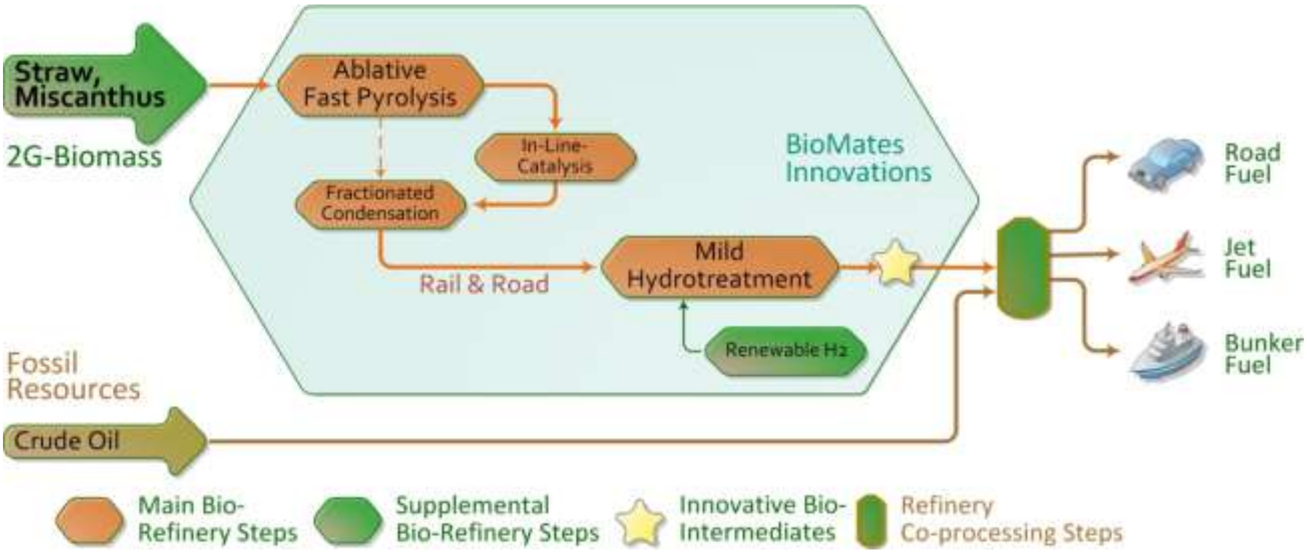

Figure 1: The BioMates-concept

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*
- HyET Hydrogen, 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

This report compiles results and explaining text sections already presented in the deliverables D1.1/D04 “Straight-run AFP products from straw & miscanthus” and D1.2/D06 “Advanced-AFP products from straw & miscanthus”, supplemented by additional results.

All products were derived from Ablative Fast Pyrolysis (AFP) in Fraunhofer UMSICHT’s TRL4-AFP-plant, described in the said deliverables.

The pyrolysis liquids from the used agricultural feedstock types either undergo a phase-separation (in single-stage condensation) or are directly gained as aqueous and tarry product (in staged condensation with appropriate process parameters). In any case, only the tarry phase / the tarry product is hereafter referred to as **“bio-oil”** , because only the tarry phase can be used for the further main process steps within the BioMates concept. Aqueous phase and bio-oil together, derived with single-stage condensation, are called “total product”.

In addition to the scope defined by the title of this deliverable, properties of some pyrolysis chars, derived as by-products, are presented.

All presented properties were derived by analytics within the BioMates-project.

3. Approach

Proximate (water content, ash content, volatile matter, fixed carbon, heating value) and ultimate (CHNO) analyses were performed on the two feedstock materials under consideration in the BioMates project. Additionally, the elemental composition regarding sodium, potassium, sulphur, chlorine and phosphorus was analysed. All feedstock analyses were performed at Fraunhofer UMSICHT. Main results are contained in the deliverable report D1.1/D04.

Many samples of AFP bio-oil from different operating conditions and condensation/vapour upgrade configurations were collected and analysed. Standard analyses performed at Fraunhofer UMSICHT for all samples were determination of water content with Karl-Fischer method, determination of total acid number TAN following ASTM D664 method adapted to bio-oils, determination of kinematic viscosity, determination of heating value and ultimate (CHNO) analysis. Additionally, the elemental composition regarding sodium, potassium, sulphur, chlorine and phosphorus was measured for the majority of samples.

At the beginning of the project, about 40 samples were sent to Thuenen-Institut for Wood Research in Hamburg, Germany, for a detailed GC-MS/FID analysis to identify the composition of the bio-oil by compounds and aggregate the results for several compound families like sugars, aldehydes, ketones, phenols, etc. In parallel, Fraunhofer UMSICHT built up own capacity to perform GC-MS/FID analysis itself.

The first results of analytical work are included in deliverable reports D1.1/D04 and the (provisional) deliverable report D1.2/D06.

UCTP also made some additional analyses using orbitrap mass spectroscopy. The results of these measurements can be found in the joint publication “Application of orbitrap mass spectrometry for analysis of model bio-oil compounds and fast pyrolysis bio-oils from different biomass sources”, Journal of Analytical and Applied Pyrolysis 124 (2017), pp. 230–238.

Several samples of char by-product from the AFP reactor and the filter were analysed at Fraunhofer UMSICHT. The values determined were ultimate and proximate analyses, additional elemental analyses as for the feedstock materials, and heating value.

Permanent gases remaining after the condensation train were analysed for O_2, H_2, CH_4, CO and CO_2 content by continuous non-dispersive infrared analysers, paramagnetic analyser (for O_2) and heat conductivity analyser (for H_2). For some experiments, gas samples were taken and analysed by GS/FID in order to determine the content of higher hydrocarbons (C_{2+}).

The specific surface area (BET surface area) and pore volume, which are important parameters of all catalysts, were determined by nitrogen physisorption.

4. Analytics of 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 properties

	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. Analytics of in-line catalysts

The applied in-line catalysts were analysed by complete N_2-isotherm adsorption performed in a *3Flex Surface Characterization Analyzer*, supplied by Micromeritics[1]. Table 1 provides selected properties, derived by this method.

[1] Micromeritics Instrument Corporation, Norcross, Georgia, U.S.A, www.micromeritics.com

Table 2: Selected properties of in-line catalysts, determined by N_2-isotherm adsorption

		Diameter [mm]	time on-stream (h)	Specific surface area (BET) [m²/g]	Single point adsorption total pore volume[b] [cm³/g]	Average pore diameter [nm]
SC40[a]	fresh	4.0	-	1994	1.11	2.30
	used		21	nd	nd	nd
SC44[a]	fresh	4.4	-	1431	0.74	2.06
	used		10.5	8	0.01	2.82
γ-Al_2O_3	fresh	3.2	-	260	0.84	13.00
	used		9	85	0.21	9.98
HZSM-5	fresh	2.0	-	347	0.34	3.92
	used		10.5	46	0.08	6.48
HZSM-5 /5%Ni	fresh	2.0	-	321	0.31	3.85
	used		12	nd	nd	nd
HZSM-5 /10%Ni	fresh	2.0	-	293	0.27	3.71
	used		10.5	nd	nd	nd

[a] SC40 and SC44 are commercial activated carbons, provided by Silcarbon[2]

[b] determined at p/p° = 0,990000000

nd: not detected

6. Analytics of AFP products

6.1. Liquid products

6.1.1. APF with single-stage condensation

The results of analytics of the main products, derived from APF with single-stage condensation, are listed in Table 3 (bio-oil) and Table 4 (char). Many values for the bio-oil have been determined by Fraunhofer directly after the production and additionally by UCTP after arrival of the samples in Prague. Some values match quite well and others show large differences, like the amount of Carbon and consequently Oxygen present in the liquid product from miscanthus pyrolysis. The reason for these deviations could not yet be explained. One possible reason could be the comparatively high amount of fly ash and fly char in the delivered miscanthus-based bio-oil, which might catalyse reactions during transport and storage.

[2] Silcarbon Aktivkohle GmbH, Kirchhundem, Germany, www.silcarbon.eu

Table 3: Properties of the bio-oils from straight-run AFP

	Wheat / barley straw		Miscanthus	
	Fraunhofer	UCTP	Fraunhofer	UCTP
Proximate analysis				
water (wt.%) according KF-titration	20.5	22.4	21.0	21.3
TAN (mg KOH/g) according ASTM D664	58	99	74	213
TAN (mg KOH/g) at buffer pH 11	185	Nd	243	
CAN (mg KOH/g) according to bio-oils method	nd	54	nd	65
kin. viscosity (mm^2/s, 20 °C)	725	884	Nd	903
kin. viscosity (mm^2/s, 50 °C)	55	(117*)	nd	(215*)
density (g/mL, 20 °C)	1.10	1.10	1.14	1.12
flash point – PMFP (°C)	nd	140	nd	215
HHV (MJ/kg)	23.6	23.3		21.3
Ultimate analysis (dry matter)				
C (wt.%)	66.7	67.4	49.0	65.3
H (wt.%)	6.7	10.6	7.8	7.1
N (wt.%)	0.8	1.0	0.4	0.2
O (wt.%) calculated by diff.	25.8	21.0	42.8	27.3
S (ppm)	553	570	Nd	nd
Cl (ppm)	245	nd	nd	Nd

nd: not determined
*: at 40 °C

Table 4: Properties of product-char analysis (reactor- and filter-char) from straight-run AFP

	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

6.1.2. APF with staged condensation

The results of analytics of the main liquid products, derived from APF with staged condensation (advanced-AFP liquid products), are listed in **Fehler! Verweisquelle konnte nicht gefunden werden.**.

Table 5: Analytical results of the advanced liquid products – stage 1 of staged condensation

	wheat / barley straw		miscanthus
	Fraunhofer	UCTP	
Proximate analysis			
water (wt.-%) according KF-titration	19.7	19.7	20.7
CAN (mg KOH/g) according ASTM D664	nd	81.0	nd
density (g/mL, 20 °C)	1.1	1.13	1.2
HHV (MJ/kg)	22.3	25.0	20.3
Solids (wt.%) according ASTM D7579[1]	0.4	nd	0.9
Ultimate analysis (including dissolved water)			
C (wt.-%)	51.2	55.1	48.3
H (wt.-%)	7.9	8.1	7.3
N (wt.-%)	0.8	0.6	0.2
O[2] (wt.-%) calculated by diff.	40.1	36.2	43.6
S (ppm)	450	nd	200
Cl (ppm)	240	nd	340
GC-MS/FID (wt.-%)			
Acids[3]	7.0	nd	7.86
Ethylene glycol	0.8	nd	< 0.4
Ketones[4]	4.2	nd	7.05
Furans[5]	0.5	nd	0.88
Phenols[6]	0.8	nd	2.3
Guaiacols[7]	2.1	nd	2.13
Syringols[8]	1.0	nd	1.96
Levoglucosan	1.2	nd	3.83

nd: not determined

[1] solvent: methanol/dichlormethane 1:1

[2] O (wt.%) = 100 (wt.-%) – C (wt.-%) – H (wt.-%) – N (wt.-%)

[3] Acetic acid; Propionic acid

[4] 1-Hydroxy-2-propanone; 1-Hydroxybutan-2-one; 2-Hydroxy-3-methyl-2-cyclopenten-1-one

[5] 2-Furanmethanol; 2(5H)-Furanone

[6] Phenol; 4-Ethylphenol

[7] 2-Methoxyphenol; 4-Ethyl-2-methoxyphenol; Isoeugenol trans; Vanillin

[8] 2,6-Dimethoxyphenol; 4-Ethyl-2,6-dimethoxyphenol

The measured data for Miscanthus based bio-oil from four different containers are in good agreement with some minor deviations that are a consequence of difficulties with sampling of bio-oil samples, i.e. with obtaining always a homogeneous representative sample, like shown in Table 6. This is particularly an issue when determining the elemental composition of the samples as small sample quantities are used for the analysis.

Table 6: Variability of bio-oils properties and compositions

Proximate analysis	Analytical sample (PYTEC 156-170)	Can. 1-1 (PYTEC 156-170)	Can. 1-4 (PYTEC 156-170)	Can. 2-8 (PYTEC 156-170)
Density at 15 °C (g/cm3)	1.120	nd	nd	nd
Density at 20 °C (g/cm3)	1.119	1.119	nd	nd
Density at 40 °C (g/cm3)	1.096	1.094	1.103	1.109
Kin. viscosity at 20 °C (mm2/s)	903.20	nd	nd	nd
Kin. viscosity at 40 °C (mm2/s)	215.20		224.20	205.20
Pour point (°C)		-6	-6	-6
Water (wt. %.)	21.28	21.46	21.15	nd
Micro Conradson carbonisation residue (wt. %.)	19.0	19.0	19.0	19.0
Total acid number (mg KOH/g)	210.0	214.2	216.1	211.7
Carboxylic acid number (mg KOH/g)*	65.1	64.9	65.7	65.0
Acid number as acetic acid (wt. %)	7.0	6.9	7.0	7.0
Higher heating value (MJ/kg)	21.55	21.24	21.52	20.74
Lower heating value (MJ/kg)	19.81	19.52	19.79	19.05
Solids content (wt. %)	1.48	nd	nd	nd
Elemental analysis of original samples				
C (wt. %.)	51.11	53.88	49.22	51.20
H (wt. %.)	8.01	7.92	7.95	7.78
S (wt. %.)	0.02	0.02	0.02	0.02
N (wt. %.)	0.18	0.18	0.17	0.20
O (wt. %.) - calculated to 100 %	40.69	38.00	42.65	40.80

* special method for bio-oils nd: not determined

6.2. Solid by-products

Analytics of solid by-products (pyrolysis coke) will be reported in the dedicated Deliverable D20/D1.5 “Report on evaluation of by-product utilization pathways”.

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

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