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Biomass based energy intermediates boosting biofuel production

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Deliverable

Protocol MS2
Product range from fast and catalytic pyrolysis and hydrothermal carbonization

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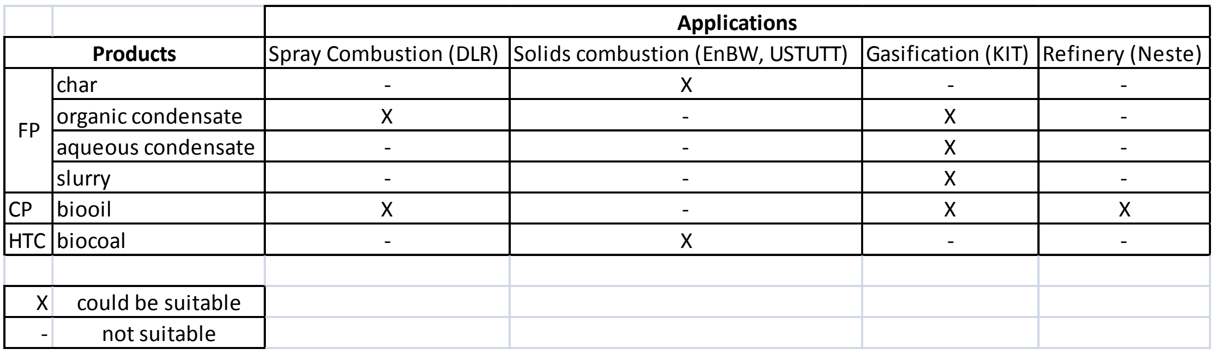
Publishable Summary

This report summarizes the actual status of the knowledge about the possible energy carriers from the three biomass conversion technologies studied within BioBoost. Their range is from liquids (biooils) via slurry and pastes (mixtures of fast pyrolysis oils and char) to solids (HTC coals and fast pyrolysis char). Given the specifications made in deliverable D5.1 “Energy carrier specifications for utilization in heat & power, gasification, refinery and chemical industry”, a rough estimation of the applicability of the respective energy carriers can be made; see Tab. 1.

Tab. 1: Estimation of suitability of energy carriers for different applications.



		Applications			
Products		Spray Combustion (DLR)	Solids combustion (EnBW, USTUTT)	Gasification (KIT)	Refinery (Neste)
FP	char	-	X	-	-
	organic condensate	X	-	X	-
	aqueous condensate	-	-	X	-
	slurry	-	-	X	-
CP	biooil	X	-	X	X
HTC	biocoal	-	X	-	-

X could be suitable

\- not suitable

Table of Content

Report

1 Introduction

In this deliverable, the range of products from the three conversion technologies fast pyrolysis (FP), catalytic pyrolysis (CP) and hydrothermal cabonization (HTC) shall be identified. These technologies yield products that could be used “as received”, that means as pyrolysis char and oil or biocoal, or further processed in order to fulfil certain physical and chemical requirements. The requirements among others are given by the handling and storage procedures and the end-use, i.e. application. In BioBoost, the transport of the energy carriers from decentralized conversion plants to centralized applications as well as the utilization in large scale gasification, combustion for the production of heat and power and in refinery are investigated. One outcome of the project shall be the determination of the most suitable, feasible and economic energy carriers.

2 Energy carrier range from different conversion processes

For the three decentralized conversion technologies involved in BioBoost, the actual considerations for the energy carriers are made separately for each technology in this chapter.

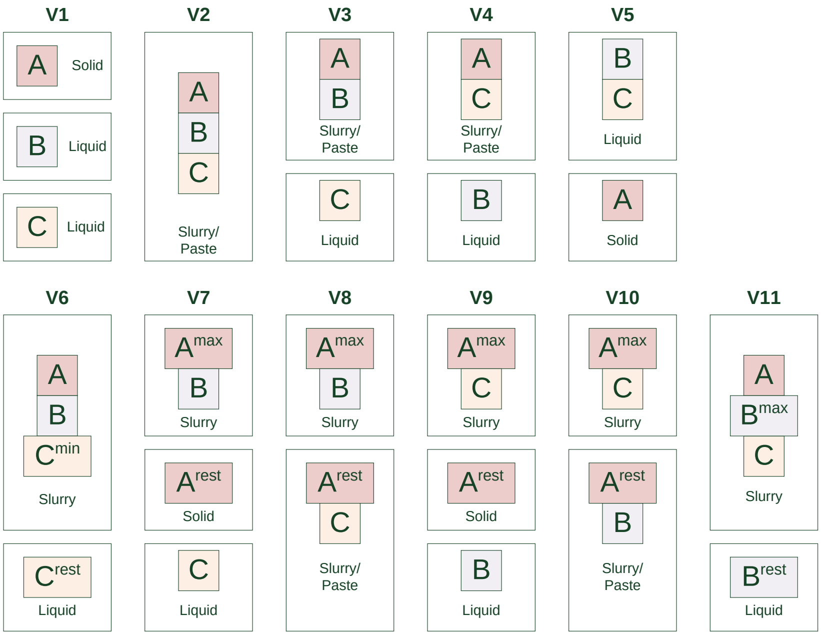
2.1 Fast pyrolysis (KIT)

The products of the fast pyrolysis process are recovered and separated via cyclones and condensers yielding three different fractions. There is a solid fraction – the char – and two different liquid condensates consisting of pyrolysis oil.
Product fractions:

- char
- pyrolysis oil:
    - aqueous condensate (mainly water with organics),
    - organic condensate (mainly organics with water)

Product variants

The fractions listed above can be handled, stored and transported in their original form or be mixed to form other energy carriers like slurries or pastes.
The following figure illustrates different variants of energy carriers.



KEY:	
Sign	**Meaning**
A	Char as received
A^{max}	maximum amount of char for pump- and flowable slurry
A^{rest}	rest of char not mixed into slurry ($A^{rest}=A-A^{max}$)
B	organic condensate as received
B^{max}	maximum amount of organic condensate for pump- and flowable slurry
B^{rest}	rest of organic condensate ($B^{rest}=B-B^{max}$)
C	aqueous condensate as received
C^{min}	minimum amount of aqueous condensate for pump- and flowable slurry

Fig. 1: Product fractions and possible variants of their mixtures. V2-V5: Mixing the entire amounts of the respective fractions. V6-V11: Mixing the products in a way, that a pump- and flowable slurry is produced.

The first variant (V1) would mean, that char, organic and aqueous condensate are handled separately; in that way one pathway for solid and two for liquid material would result. In the second variant, (V2), the whole amount of products would be mixed to form one energy carrier. This would be a slurry or paste, depending on the respective yields of product fractions and their chemical and physical properties. In V3 to V5, there would be a mix of two product fractions and the residual one, thus having two energy carriers per each of these variants.

A high yield of char and a high viscosity of the pyrolysis oil could result in a paste that is not flowable. If the objective target for an energy carrier is a free-flowing and pumpable slurry, it might be necessary to adjust the amounts of the product fractions that are mixed together. This is shown in the variants V6 to V11. In V6, the desired energy carrier would be a slurry with little water and thus high heating value; therefore, the whole amount of char and organic condensate are mixed with the minimum amount of aqueous condensate necessary for assuring the pump- and flowability. The rest of the aqueous condensate would be handled separately.

As can be seen from the figure, there are various possibilities of product mixtures.

Product specification

The desired forms and properties of the energy carrier are dependent on the final technical application it shall be used in.

For the products of the fast pyrolysis, the following applications may be possible:

- gasification of slurries/pastes in order to produce fuels and chemicals via syngas
- combustion of pyrolysis oil for the production of heat and power
- combustion of the char for the production of heat and power.

Energy carrier specifications for these applications are documented in the report D5.1.

These specifications and the fact that the energy carriers need to be transported between the fast pyrolysis plants and the technical applications lead to a variety of properties of interest related to the energy carriers. Techniques and requirements for production, handling, storage and transport need to be defined in order to assess the applicability and economy of the energy carriers.

Therefore, the following energy carrier properties are of special interest:

- High heating value,
- bulk density,
- energetic density per volume,
- char, ash and water content
- preparation techniques,
- hazard potential,
- stability, sedimentation,
- viscosity, flow properties, pumpability, acidity

The following table shows important properties of a selection of different possible energy carriers.

Tab. 2: Properties of a selection of possible energy carriers.

Energy carrier number	1	2	3	4	5	6	7	8	9	10	11	12	13
	straw char unmilled	**straw char milled**	**organic condensate as received**	**heavy organic fraction from organic condensate**	**light organic fraction from organic condensate**	**aqueous condensate as received**	**slurry 1 - all condensates + straw char milled**	**slurry 2 - organic condensate + straw char unmilled**	**slurry 3 - organic condensate + straw char milled**	**slurry 4 - aqueous condensate + straw char unmilled**	**slurry 5 - aqueous condensate + straw char milled**	**paste 1 - organic condensate + straw char milled**	**paste 2 - aqueous condensate + straw char milled**
related to variant no. of Fig.1	**V1,V5,V7, V9**	**V1,V5,V7, V9**	**V1,V4,V9, V11**	**V1,V4,V9, V11**	**V1,V4,V9, V11**	**V1,V3,V6, V7**	**V2**	**V7,V8**	**V7,V8**	**V9,V10**	**V9,V10**	**V3**	**V4**
HHV (MJ/kg)	18 - 26	18 - 26	~ 20	~ 25	~ 12	~ 5	14 - 17	19 - 21	19 - 21	7 - 9	9 - 11	18 - 24	12 - 18
bulk density (kg/m³)	300 - 500	300 -600	~ 1200	~ 1200	~ 1100	~ 1000	1250 - 1300	1250 - 1300	1250 - 1300	1100 - 1150	1100 - 1200	1200 - 1600	1200 - 1400
energetic density (GJ/m³)	5 - 13	5 - 16	~ 24	~ 30	~ 13	~ 5	17 - 22	24 - 28	24 - 28	8 - 11	9 - 14	22 - 38	15 - 25
char content (wt%)	100	100	< 10	< 15	0	0	33	15	20	20	30	60	60
ash content (wt%)	20 - 40	20 - 40	~ 2	~ 2	0	0	7 - 14	4 - 8	5 - 10	4 - 8	6 - 12	12 - 25	12 - 24
water content (wt%)	0	0	15 - 40	8 - 15	40 - 55	75 - 85	29 - 42	12 - 34	12 - 32	60 - 68	52 - 60	6 - 16	30 - 34
preparation	possibly pelletizing	milling; possibly pelletizing	none	settling		none	milling; colloidal mixer	colloidal mixer	milling; colloidal mixer	colloidal mixer	milling; colloidal mixer	milling; kneader or extruder	milling; kneader or extruder
hazard potential	highly flammable; pyrophoric (self ignition > 125 °C); dust explosion; inhalation of fine particles		corrosive, highly flammable, harmful to health, contains mutagenous and toxic substances; leakage		corrosive, harmful to health, contains mutagenous, toxic and flammable substances; leakage		corrosive, flammable, harmful to health, contains mutagenous and toxic substances; leakage			corrosive, harmful to health, contains flammable, mutagenous and toxic substances; leakage		corrosive, flammable, harmful to health, contains mutagenous and toxic substances; no leakage	
stability	stable		unstable; depends on ethylene glycole and water content	almost stable, viscosity increase over time	stable		limited					stable	
sedimentation	none		depends on solid content		none		yes; characterisation of sedimentation to be investigated					none	
viscosity, flow properties, pumpability	powder properties; dependent on density and particle size distribution; particle size distribution 1 mm to some µm; screw conveyors		temperature dependent, pumpable with screw and plunger pumps		similar to water, corrosion-resistant pumps		flowable, temperature dependent, pumpable with screw and plunger pumps					not flowable at ambient temperature, conveyed via screw conveyors and extruders	

In the table, the energy carrier (EC) numbers 1, 3 and 6 correspond to the product fractions as recovered in the pilot plant. If the char is milled, some of the properties (e.g. bulk density) change, therefore the milled char is shown here as EC 2. The organic condensate can separate into a heavy and a light phase, depending on

process conditions in the pyrolysis plant. These fractions are presented as EC 4 and EC 5. In Fig. 1, they are not listed for reasons of clarity and comprehensibility. For the same reason, the table restricts on just a few examples (EC 7 to 13) for the theoretically possible mixtures of the before specified single substances (EC 1 to 6).
EC 7 is a free-flowing and pumpable slurry with the whole amount of all product fractions with the assumption that each fraction makes up 33 wt% in the mixture and without phase separation. EC 8 to 11 are slurries of the organic (assumption: no phase separation) respectively the aqueous condensate with a maximum amount of char to meet the target of flow- and pumpability. The contents of char given in the table are first estimates that need to be evaluated. Sedimentation of the char could lead to problems when handling the slurries after a certain storage time. A solid sediment in vessels or tank should be avoided as it could block the outlets.
Mixture of char and condensate(s) with a certain solid content are not free-flowing but paste-like. Ideally, the pastes are stable and therefore well-storable. Another advantage of pastes is that in case of a crack in a tank, there wouldn't be a leakage.
In the table, EC12 and 13 are examples of pastes with an assumed char content of 60 %. Experimental investigations of the production of pastes with kneaders and extruders shall show the feasibility and applicability of this form of energy carrier.

At this stage of the project, it is not possible to exclude certain options of energy carriers. In order to reduce complexity and to give reference cases, the following energy carriers are suggested:

- char (as received and milled)
- organic condensate of pyrolysis oil as received
- aqueous condensate of pyrolysis oil as received
- pump- and flowable slurry of both pyrolysis oil condensates and milled char

Table 3 summarizes the range of application for the stated energy carriers in relation with the statements made in report D5.1. For example, for the spray combustion investigated by DLR, just the organic condensate seems appropriate due to a sufficient heating value whereas the HHV of aqueous condensate would be too low. Solid char and a highly viscous slurry containing lots of particulate matter would not be feasible for the concept of spray combustion.
For the combustion of solids, just the pyrolysis char can be utilized because of the nature of such incinerators (feeding system etc.).
The gasifier should be able to handle all energy carriers that can be atomized. A low heating value of an inlet stream would be compensated by other inlet streams with higher heating values.
For the utilization in a refinery, none of the products seems appropriate. The water content of the pyrolysis oils produced by KIT's fast pyrolysis is too high.

Tab. 3: Overview of the expected suitability of the reference case energy carriers for different applications.

	Applications			
Products	Spray Combustion (DLR)	Solids combustion (EnBW, USTUTT)	Gasification (KIT)	Refinery (Neste)
char	-	X	-	-
organic condensate	X	-	X	-
aqueous condensate	-	-	X	-
slurry	-	-	X	-

X	could be suitable
-	not suitable

2.2 Catalytic pyrolysis (CERTH)

The main product that it is produced from catalytic fast pyrolysis is the catalytic biooil. An aqueous phase is also produced that might be used for extraction of some chemicals (in WP3). However, we can consider only the catalytic biooil as the main product from this pathway. Gaseous products (mainly CO and CO_2) can be used for recycling or for heat production. Solid products (char and coke) are consumed within the process for energy production in the regenerator.

The physical and chemical properties of the catalytic biooil depend strongly on the type of catalyst and on the operating conditions of the process (mainly temperature, residence time and catalyst/biomass-C/B- ratio). Depending on catalyst activity we can make oil with an oxygen range between 30-15%wt at T=500°C and a C/B ratio=15. In the table below we summarize the properties of the biooil with 2 different ranges of oxygen content.

Tab. 4: Important parameters of the biooil from catalytic pyrolysis with two different catalysts.

	ZSM-5	**Silica Sol**
H_2O content, %wt	6.5	7.8
C, %wt (dry basis)	74.5	71.5
H, %wt (dry basis)	7.5	7.1
O, %wt (dry basis)	18.0	21.5
TAN, mgKOH/g	40	49
MCRT	18.4	17.4
HHV, MJ/Kg	29.5	27.2
Density, g/cm^3	1.12	1.14
Pour point, °C	-39	-
Flash point, °C	29	-
Viscosity, cSt	13.7	16.8

In general the handling, storage and transport issues of the catalytic biooil could be similar to that of the conventional heavy fuels. Of course it is preferable not to heat it above 60°C, in order to avoid secondary reactions that could alter its composition. It can be stored at room temperature, however it is best to store it in cool rooms (~4°C) and in any case away from direct sunlight, in order to avoid reactions as mentioned above.

Regarding its corrosivity it is classified as 1a at the copper corrosion tests, which means that it induces minimum corrosivity. Toxicity data are not available for living organisms. However, its high phenolic concentration renders it inappropriate for prolonged direct contact with living organisms or aqueous systems. For hazard identification it could be identified probably as Xn, Xi and N.

Regarding degradation (shelf life), accelerated ageing tests performed in BIOBOOST showed an increase in the biooil's viscosity but no deposition of material was observed. However it is suspected to form phases after storage for more than a year. In general catalytic biooil can be stored without any difficulties.

Catalytic biooil can be shipped and/or transported by similar safety measures as heavy fuels. For cleaning the containers, they should be rinsed with acetone or similar polar solvent and afterwards cleaned with water. Regarding tank material, since it is not suspected for corrosion at normal temperatures regular stainless steel should be sufficient.

The use of the catalytic biooil in a refinery is investigated within this project. The use in spray combustion and gasification could also be a possible application, but isn't pursued in the project.

Concerning the extraction of chemicals from CP biooil.

The use of a catalyst during the pyrolysis of biomass has an important effect on the composition of the resulting CP biooil. Depending on the catalyst's properties, the CP biooil could be enriched in a certain class of compounds, e.g. aromatic hydrocarbons, phenols etc. Also, the depolymerisation of the biomass proceeds to a greater extent and as a result the biooil contains less macromolecules and insoluble compounds, allowing for an easier handling of the material during extraction processes. Based on the above, it is concluded that CP biooil is a more promising precursor for the extraction of chemicals than the FP biooil

2.3 Hydrothermal carbonization (AVACO2)

The products produced by the HTC such as biocoal and biochar after liquid/solid separation are easy to handle. There are possibilities to produce pellets, powder, briquettes, or/and gasify them. Furthermore the biocoal can be mixed with other biocoal qualities even biocoals from different biomasses. The combustion of the biocoal for the production of heat and power is investigated within this project.

Once the biocoal is transformed, it can be stored without any difficulties. However if the biocoal is to be stored as a powder, safety measures need to be implemented, because biocoal powder is explosive. The transport of biocoal is not problematic; it can be shipped and/or transported by lorries (safety measures apply for biocoal powder).

The selection of the following biomasses is based on several criteria:

- technical feasibility: it should be possible to handle the biomass easily for the usage in an HTC plant. This is possible for all of the suggested biomasses, with one exception: municipal waste has to be pre-treated in order to separate organic from inorganic waste. If this is done, this biomass works perfectly.
- analytical data: by analytical data, we mean the characterisation documented in D2.1 (p 21 ff.). Sewage sludge is added here, because of economic criteria
- availability: we can only partially follow the research results of WP1, because there are limitations to the availability of data. Even though brewery molasses are mentioned on page 43, the availability could not be specified. However, based on AVA-CO2's contacts to several clients from the brewery industry, we know that there is a potential of several dozens of HTC plants in Europe. This use case is especially interesting, because it is very economically feasible, if a co-location concept is applied. The same is true for sewage sludge, not mentioned in WP1, but interesting for economic reasons.
- economic analysis: economic analysis relates to several issues, which are only estimated at this stage of analysis. Most biomasses are not available for free, in fact prices are rising. Therefore, AVA-CO2 is focussing heavily on biomasses, which cost nothing, or which are paid for, if disposed properly. Logistics costs are also of importance. Both, municipal waste and sewage sludge are excellent examples. If big municipalities are chosen, logistics costs could be reduced to zero (not taking into account the garbage collection, which

has to be done anyway). The same is true for breweries spent, which not only reduces biomass and logistics costs to zero, but also could reduce energy and infrastructure costs dramatically, if the plant is located on the premises of breweries.

Taking into account these criteria, the following biomasses are the biomasses of choice for hydrothermal carbonization:

Tab. 5: Comparison of high heating values (HHV) for different biomasses and the resulting biocoals.

	Brewery Spent Grain	Straw	Municipal Waste	Sewage Sludge
Biomass HHV *[MJ/kg DM]*	21,6	18,07	9,5	13,6
Biocoal HHV *[MJ/kg DM]*	29,8	24,4	24,2	15,5

AVA-CO2 also has set up a project to gain and extract 5-HMF from the HTC process. Analysis shows, that 5-HMF is present in the process water, but only in negligible amounts (ca. 5-25 ml per liter HTC process water). This amount of 5-HMF is economically not interesting for extraction and separation. However, modifying the process parameters allows the substantial increase of 5-HMF. Together with KIT (IKFT) the parameters have been tested extensively, accompanied by economic analysis. Both, lab tests and scale up tests at K3 provide a range of 8-12 min residence time as optimal for maximal 5-HMF production. Yield is substantial (up to 5gr per liter) and economically interesting. There are also furfurals and oligomers in the liquid. AVA-CO2 has tested several methods for the extraction and separation of 5-HMF. Chloroform proved to be the most effective solvent, even though there are rather draconic restrictions for commercial use. At this point of time, AVA-CO2 reaches a purity of 5-HMF of 70-85 %. Industry standard is 99 %. Therefore, additional steps have to be taken to match market criteria, but the outlook is very promising.

On the other hand, the dramatic reduction of residence time (HTC for coal production is between 4 and 5 hours, whereas 5-HMF is generated below 15 minutes) is not enough for coal production. The resulting slurry from 5-HMF production is just added to new feedstock for carbonization. This rather pragmatic approach at this level of research is possible due to the small amounts added to large volume coal production. So far, it can neither be stated, if this is a viable solution for an integrated coal and HMF plant, nor is it possible to find a path to an integrated HTC-biorefinery, which produces coal and 5-HMF (and possibly furfurals) within an integrated approach.

3 Conclusions

For each conversion technology, the possible energy carriers and their possible applications have been identified. For the biooil from catalytic pyrolysis the base case would be the use in a refinery. The biocoal produced via HTC shall be used in combustion for heat and power production. The product range from fast pyrolysis is much more complex. The three product fractions *pyrolysis char, aqueous and organic condensate of the pyrolysis oil* cannot only be used separately but several mixture variants show promise. At this stage of the project, it is not possible to exclude certain options of energy carriers. The energy carriers from fast pyrolysis may be suitable for spray and solids combustion and gasification.

4 Future Work

For HTC and CP, the main work consists of optimizing the process conditions themselves in order to meet the specifications of the above mentioned applications. For the case of energy carriers from FP, more experiments such as feasibility studies on the production and stability of slurries and pastes with certain solids-to-liquid-ratios will be necessary.

5 Consortium decision

Based on the conclusions above the technology providers KIT, CERTH and AVA-CO2 propose to the consortium to proceed with the following energy carriers.

For the fast pyrolysis the following energy carriers are suggested:

- char (as received and milled)
- organic condensate of pyrolysis oil as received
- aqueous condensate of pyrolysis oil as received
- pump- and flowable slurry of both pyrolysis oil condensates and milled char.

These energy carriers may be suitable for spray and solids combustion and gasification.

For the HTC process the biocoal shall be used in combustion for heat and power production.

For the catalytic pyrolysis the catalytic biooil would be used in a refinery.

The consortium gave their agreement based on the results outlined in this deliverable 2.2, to proceed with the above listed energy carriers to production, handling, storage and transport validation tests and further use these energy carriers in demonstration applications.