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Biomass based energy intermediates boosting biofuel production

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Deliverable

Energy carrier specifications for utilization in heat & power, gasification, refinery and chemical industry

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Publishable Summary

The overall objective of the BioBoost project is to pave the way for de-central conversion of biomass to optimised, high energy density carriers, which can be utilised in large scale applications for the production of transportation fuels and chemicals or utilisation directly in combined heat and power (CHP) plants.

Therefore, the de-central conversion of dry and wet residual biomass and waste as feedstock by fast pyrolysis, catalytic pyrolysis and hydrothermal conversion to the intermediate energy carriers catalytic oil (from catalytic pyrolysis), biocoal (from hydrothermal conversion) and bio-syncrude (mixture of biocoal and liquid (organic and aqueous) phases from fast pyrolysis) is studied. These energy carriers are suitable for large-scale gasification, but due to additional applications, the economics of the whole chain may be improved.

These additional applications include extraction of by-products, upgrade in refineries to transportation fuels via hydro treatment or catalytic cracking, gasification to synthesis gas, usable for e.g. Fischer-Tropsch-Synthesis or direct burning of the intermediate energy carriers biocoal and the liquid phases of the slurry in CHP.

This report summarises the energy carrier specifications which need to be met for utilisation.

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Report

1 Introduction

The BioBoost project aims to pave the way for de-central conversion of biomass to optimised high energy density carriers.
Therefore, the project investigates the production, characteristics and logistics of different bioenergy carriers from de-central fast and catalytic pyrolysis as well as hydrothermal conversion. All intermediate energy carriers which result from these conversion technologies (biocoal, catalytic oil and bio-syncrude) are suitable for a large-scale gasification. With additional applications of these intermediate energy carriers the economics of the whole chain may be improved. As additional applications, extraction of by-products (from catalytic oil as well as from process water of hydrothermal carbonization), upgrade in refineries via hydro treatment or catalytic cracking, gasification and direct use of the intermediate energy carriers biocoal and the liquid phases of the slurry for means of combustion in combined heat and power plants come into consideration.

In this deliverable, the techno-economic requirements concerning the application of the intermediate energy carriers in combustion for heat and power, in gasification, for upgrade in refineries and extraction of by-products for chemical industry are specified based on the currently available know-how. Some values may only be defined when more tests will be executed.

2 Energy carrier specifications for different utilization paths of intermediate energy carriers

Resulting from de-central conversion of biomass via fast or catalytic pyrolysis and hydrothermal conversion, the intermediate energy carriers biocoal, catalytic oil and bio-syncrude can be utilized in different ways.

In the following chapters, the energy carrier specifications which need to be kept for different applications (extraction of by-products, upgrade in refineries, gasification and direct combustion) are specified.

Since the specifications are based on the currently available know-how, they might be too strict. But on the other hand, it cannot be guaranteed that every application will work properly, even when the listed specifications will be met.

2.1 Combustion – Biocoal

In order to use the biocoal in commercial CHP plants of EnBW without implementing major modifications, the properties of the biocoal must be similar to those of the standard fuel (hard coal).

The following table summarizes the specifications which need to be kept for combustion purposes of the bio-char in CHP plants based on hard coal.

Table 1: Specifications of biocoal for combustion purposes and reference coal

Property	Unit	Requirement for bio-char	Reference coal (hard coal, US coal)
Heating Value	MJ/kg	24 – 29	29,4
Ash Content	%wt	8 – 12	9,8
Water Content	%wt	7 – 12	11,2
Sulphur	%wt	< 1	0,5
Nitrogen	%wt	< 1.8	1,7
Volatiles	%wt	22 – 40	39,2
Grain Size	mm	50	
Grindability	°H	45 – 65	45
Ash Fusion Temperatures			
Softening Temperature	°C	> 1250	1454
Hemispherical Temperature	°C	> 1300	1477
Self-ignition Temperature	°C	> 300	> 300
Chlorine (waf)	%wt	< 0.1	0,01
CaO	%wt	< 2	0,38
Alkalines	%wt	< 0.5	0,23
Phosphor	%wt	< 0.1	0,09

Regarding the economic scale, the price of the bio-char must be lower than the price for hard coal (for comparison, the price for a ton of hard coal incl. insurance, until port of destination).

For a complete replacement of the hard coal with the bio-char, an amount of up to 300 tons per hour (depending on the heating value of the bio-char) for a CHP plant with an electrical capacity of app. 900 MW is necessary.

Properties regarding transport, handling and storage must be similar to hard coal. That means, transport of bio-char by railway and ship must be possible without any additional measures like inerting.

Considering the possible risks of the utilization of bio-char in a commercial CHP plant, the self-ignition temperature is of crucial importance. Since the coal is milled prior to combustion and the temperature within the coal mill can be above 250°C, a low self-ignition temperature of the bio-char possesses a major risk for the power plant.

2.2 Combustion – Liquid phases of the slurry

Defining specifications of a potential fuel prior to having started detailed studies is demanding and can only be regarded as an initial guess. Thus, the below listed specifications might appear too strict in future research activities during the project progress. On the other hand, with listed specifications, full functionality of the proposed combustion concept cannot be guaranteed.

Following parameters appear essential for successful spray combustion: viscosity is a sensitive issue influencing atomization of the spray. Good atomization to small droplets favors full droplet vaporization during the residence time in the combustor and subsequent combustion. Therefore, a viscosity no higher than 180 cP at 50°C (already being a challenge) is recommended. Though frequently not desirable, a two-phase emulsion (water and oil fraction) can be beneficial for spray break-up due to micro explosions, so the respective content of the “other” phase is less critical.

The other parameter of major concern is the heating value of the fuel. The FLOX® principle has proven flexibility over a wide range of gaseous fuel compositions and heating values in our institute so far. Nevertheless, low heating values required compensation by higher mass flows to provide the combustion process sufficient thermal load for sustained operation. Certain levels of heat released in the process are essential to stabilize spray combustion. So, the heating value specified below represents a compromise between what appears acceptable for the FLOX® concept and mass flow flexibility – the safe side of operability is surely the high heating value side; values above 20 MJ/kg are recommended.

Another parameter of interest is the solid content of the liquid energy carrier. Solid residuals of the pyrolysis process pose two major issues: clogging of the nozzle and insufficient burn rate when passing the combustor and resulting in soot formation. While mass content is less critical, the particle size in the fuel is sensitive. Removal of particulate matter larger than 50 µm at the end of the pyrolysis process would cancel the need for filtering for combustion. Smaller particles should minimize clogging of the nozzle and should be completely combusted.

While a laboratory experiment can handle acid fuel to a certain amount (replace corroded components after certain run times), acidity is certainly an issue when transferring the process to technical conditions. So, it does not find introduction in this document but will rather be of interest for later application.

Table 2: Specifications of liquid phases of the slurry for combustion purposes

Property	Unit	Requirement
Heating value	MJ/kg	Min 20
Dynamic viscosity at 50 °C	mPa s	Min 180
Solid residual size (preferred)	µm	Max 50

Solid residual total mass	%wt	Unspecified
Water content in oil		Unspecified*
Oil content in water		Unspecified*

* if not compromising heating value

Other criteria concern scales, handling and risks. For the FLOX® combustion experiment currently being set up a throughput of 3-5 kg/h is planned. This requires availability of roughly 20 l/day. The first shipments received from KIT for spray testing were delivered via regular freight shipping (including the required shipping formalisms for this type of chemicals) in portions of 25 l. Main risks than could occur are spills inside the laboratory covered by DLR safety provisions, or any type of event during transport which should be covered by the safety procedures detailed in the shipping documents.

2.3 **Gasification**

For the gasification process, the “base case” of energy carriers for the experiments at the test facility at KIT is in form of organic and aqueous slurries made from the products of the fast pyrolysis of wheat straw. The term bio-syncrude (slurry) designates a suspension of an aqueous and organic phase and char particles. From previous experience with the gasification of slurries consisting of pyrolysis products, the range of the most crucial parameters is known. However, as mentioned already in chapter 2.2, it is not guaranteed that these specifications will turn out to be correct for the case of our special biomass slurries in the operation of our gasifier.

Major requirements for the energy carrier are: pumpability, atomization and a sufficient heating value. For the feed of the bio-syncrude into the pressurized gasifier via pumps, viscosity must not be too high. A maximum value for the dynamic viscosity of about 1 Pa·s at 70 °C seems to be an appropriate preliminary limit. The viscosity also affects the atomization to small droplets in the gasifier, which are required for a complete conversion to gaseous products. The formation of small droplets with the help of nozzles also puts constraints to the maximum particle size of the solid particles in the bio-syncrude. Smaller particles can be gasified more rapidly, giving a higher carbon conversion. Furthermore, clogging of the nozzles due to too big particles or agglomerates must be avoided. Therefore, the maximum grain size is set to be not higher than 0.1 mm and the maximum content of solid particles may not exceed 40 wt% in the bio-syncrude.

In order to achieve a sufficient temperature in the gasifier, the energy content of the feed is an important parameter. The lower heating value of the feed should be between 13-25 MJ/kg.

Below, reference values of two feed bio-syncrudes are given that can be used for orientation.

Table 3: Specifications for gasification purposes

Property	Unit Unit	Requirement of bio-syncrude	
		“organic phase”	“aqueous phase”

Elemental analysis				
C	%wt	waf	~70	~70
H	%wt	waf	~6	~6
N	%wt	waf	~0.5	~0.5
O	%wt	waf	~22	~24
S	%wt	waf	< 0.1	< 0.1
Cl	%wt	raw	≤ 1	≤ 1
Water	%wt	raw	10-15	35-50
Ash	%wt	raw	3-10	3-10
Calorific data				
Low heating value (LHV)	MJ/kg	raw	≥ 20	≥ 10
Solids content	%wt		20-40	~40
Grain size	µm		< 100	< 100
Density	kg/m³		~1300	~1200
Dynamic viscosity @ 20 °C	Pa·s		20-60	10-15

2.4 Refineries

Although the upgrading of intermediate energy carriers produced via the catalytic pyrolysis process are superior to those produced by a thermal pyrolysis process as they have reduced water content, lower oxygen percentage, reduced acidity and are more stable, there remain risks involved when introducing these into an oil refinery.

The risks are:

1. Acidity and corrosion during storage
2. Metal impurities which reduce catalyst lifetime
3. Poor stability in storage and during heating
4. Excessive coke formation

Corrosion

A general risk in processing pyrolysis bio-oils in refinery processes is related to possible corrosion problems due to the acidic nature of bio-oils. Carbon steel – a common material in many refinery units – will not withstand acidic feeds even in low concentration. Therefore the water and acid content of the energy carrier should be minimised. But removal of water and low molecular weight acids could also remove other oxygenates which are necessary for maintaining a low viscous product. This could cause problems during shipping and storage.

Impurites

Following specifications for impurities and some physical properties have been defined for feeds to a catalytic cracking unit to give guidelines for suitable biomass derived feeds:

Table 4: Guidelines for specifications for refinery purposes

Property	**Specification test method**	**Unit**	**Requirement**
Total nitrogen	ASTM D 4629	mg/kg	max 2 000
Density at 15 °C	ASTM D 4052	kg/m^3	max 930
Sulphur content	ASTM D 4294	%wt	max 2.00
Distillation temp. 95 % vol. recovered	ASTM D 1160 or ASTM D 2887	°C	600
Water		%wt	max 2
Ni + V	ASTM D 5185	mg/kg	max 2
Fe	ASTM D 5185	mg/kg	max 2
Na	ASTM D 5185	mg/kg	max 10
Ca	ASTM D 5185	mg/kg	max 100
Si	ASTM D 5185	mg/kg	max 10
Mg		mg/kg	max 10
Pb		mg/kg	max 10
P		mg/kg	max 200

Depending on the specific catalyst used, the acceptable concentration of certain metals is very low. There will therefore be restrictions for many other elements (e.g. K, Cl and Sn). When co-feeding there is more flexibility in the requirements depending on the percentage of catalytic oil added into the fossil feed and the miscibility of the catalytic pyrolysis liquid in hydrocarbons.

In co-feeding it will be important to have a low oxygenate content product as this will be more miscible with the non-polar hydrocarbon based fossil feed. The lower the oxygen content of the catalytic oil, the higher the miscibility will be, especially in relation to amounts of aldehydes and ketones as minimizing these will also improve the stability of the pyrolysis oil. Stability is an important issue regarding storage and transportation, but also for further processing if preheating of the feed is needed.

Stability

The lower the oxygen content of the catalytic oil and especially in relation to the concentration of aldehydes and ketones, the better the stability of the catalytic liquid will be. Stability is an important issue regarding storage and transportation, but also for further processing if preheating of the feed is needed.

In summary, low oxygenate (especially acid), water and metal contents should be tried to be achieved for energy carriers to be utilised in refinery environment. At this point no specific requirements for physical properties such as viscosity, ash content, flash point, cloud point or pH can be set. More detailed analysis of catalytic pyrolysis oils and experimental tests have to be carried out. Restrictions regarding other chemical or physical properties might come up depending on the upgrading process evaluated. The need for some pre-treatment of the catalytic oil before upgrading to transportation fuels will be considered if necessary.

Tendency to Coke

Conditions to upgrade the catalytic pyrolysis intermediate energy carrier will vary depending on the process employed. The experimental results to date indicate that elevated temperatures and hydrogen pressures compared to normal hydrodesulphurization units will be required. In order to minimize coke formation under these severe conditions, an initial stabilization step will be necessary. This is best realized by exposing the liquid to hydrogen pressure under reduced temperatures for a sufficiently long duration.

Economic Scale

The appropriate scale for upgrading in an oil refinery by hydrotreating will be determined by the access to available hydrogen. As the refinery hydrogen is normally produced by steam reforming of natural gas which are capital intensive, the appropriate scale may only be determined on a case by case basis for the refineries. An appropriate level could be in the 200 to 250 MW scale and will be depending on the hydrogen consumption and the availability of hydrogen.

Availability

No data on availability is available at this time. In a refinery environment where units are interconnected and interdepent, availability of over 95% is the goal and usually well reached.

2.5 Chemical Industry

For the extraction of substances from hydrothermal carbonization process water as well as from oil from catalytic and fast pyrolysis, concentrations of the substance to be extracted need to be stable within a range of 0.5 %wt to ensure an economical extraction. The amount of surfactants needs to be considerably low to ensure phase separation during extraction.

For the extraction of furfural and / or 5-hydroxymethylfurfural from the aqueous phase of the hydrothermal carbonization process, the surface tension of the process water should not change with different process batches.

For economical extraction of phenol and guiacol from oil of catalytic pyrolysis, the concentration is required to be above 2 %wt. The same applies for a single substance to be extracted from oil from fast pyrolysis. An estimation of the economy of scale on such a process is at this moment of time not possible.

The availability of bio-oil for having a plant with relevant output of phenol is dependent on starting concentration in the bio-oil. For bulk chemical production the availability of bio-oil will be the limiting factor in the scale-up. If a phenol extraction plant from bio-oil shall produce 10 kilo tons per annum (kta) 500 kta of bio-oil with a phenol concentration of 2% need to be available.

For transporting phenol there are existing procedures which do not need to be developed new. For example, the UN 1671 Phenol solid or UN 2312 Phenol molten classification. MSDS is available at phenol producers.

3 Conclusions

Summarizing the specifications of the intermediate energy carriers for the different applications, it can be concluded, that the heating value of the biocoal and the liquid phase of the slurry should reach at least 20 MJ/kg for combustion purposes.

For the use of catalytic oil in gasification and combustion as well as for refinery purposes, it needs to be pumpable and sprayable and the acidity should be minimized.

To ensure an economical extraction, the concentrations of the desired substances need to be at least over 2 %wt (depending on the substance).

4 Future Work

In the upcoming work of WP5, the different applications for the use of the intermediate energy carriers will be analyzed in more detail.