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Biomass based energy intermediates boosting biofuel production

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Deliverable

Final report of WP2 summarizing the optimization of conversion technology processes: Pyrolysis, Catalytic Pyrolysis, Hydrothermal Carbonization

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Publishable Summary

Thermal Pyrolysis (KIT)

The objective of KIT work in Task 2.2.1 was to optimize setup and operating conditions of facilities for fast pyrolysis of dry feedstock towards an energy carrier suitable for gasification and synthesis according to the bioliq concept. Besides this reference pathway, the goal was to have a pyrolysis process with products that enable flexible use in form of different energy carriers for further energetic and material applications, generating a value addition and helping to introduce the technology to the market.

At KIT, plants for the fast pyrolysis of biogenic residues exist on lab-, test-size- and pilot-scale. Both the test-size (10 kg h^{-1} biomass feed) –in the following referred to as process demonstration unit (PDU) – and the bioliq pilot scale unit (500 kg h^{-1} biomass feed) make use of a twin screw mixer reactor.

In the original design of the PDU, solid product was separated in a first condensation step together with pyrolysis oil and water. In the framework of the bioliq-concept, this is a reasonable procedure as solid and liquid products shall be fed together to an entrained flow gasifier. A second condensation step followed, yielding an aqueous condensate, consisting mainly of water loaded with organic compounds. However, for applications beyond gasification such as combustion or the extraction of valuable components, this way of product recovery is unfavorable. As a consequence, the bioliq pilot plant (500 kg h^{-1} biomass) was set-up with a different product recovery, comprising a separation of solid particles from the hot product vapors in a cyclone followed by a two-step condensation of the vapors. In this way, a stable but viscous organic condensate with low solid and water content on the one hand, and a water-rich aqueous condensate on the other hand, can be achieved. The solids are obtained as virtually tar-free pyrolysis char particles.

In order to be able to advance the pyrolysis and product recovery process on a smaller scale, the PDU was retrofitted within BioBoost and now makes use of the optimized procedure for product recovery of the bioliq pilot plant: Recovery of separate product fractions, which allow for a flexible use in different applications. In this way, open questions and parameter studies can be investigated more efficiently and tools for the scale-up of pyrolysis plants can be developed. The reconstruction of the PDU furthermore allows a direct comparison of the two variants of product recovery.

Pyrolysis experiments have been conducted with three biomasses, wheat straw, miscanthus and scrap wood, described in BioBoost Deliverable 2.1. The results from the mass, carbon and energy balances lead to the conclusion, that during the recovery of solids and condensates in a single step as in the former setup of the PDU, follow-up reactions occur producing further solids and gases.

Both strategies of product recovery at test-size scale worked technically well. The separation of wet char crumbs shows several advantages compared to the separation of dry char powder, especially in relation to safety aspects. Opposite to this, a higher flexibility for the utilisation of the pyrolysis products is provided in case of a separate recovery of the products. Another advantage is that the organic condensate as gained in the modified PDU and bioliq-pilot plant is flowable and pumpable, i.e. to handle with standard equipment and less effort than the sticky char crumbs produced in the former setup. Despite the successful operation of the separation of char crumbs at PDU scale according to the former product recovery procedure and the fact that tar/pyrolysis oil, char as well as mixtures of these fractions are suitable as feed for gasification, the separate product recovery as utilized in the modified PDU and the pilot plant seems to be the better option. Besides an expected better scalability, the product fractions can be mixed more flexibly to a slurry and thus can be adjusted to the needs and specifications of the gasifier (BioBoost reference utilization pathway).

The yield of slurries is practically the same for all 3 biomasses due to the similar yields of gases during pyrolysis. From 1 kg of a completely dried biomass (0 wt% water), between 0.75 to 0.8 kg of slurry can be derived. However, properties vary relatively strong, especially in terms of solid and therewith ash content. Wheat straw, having an average ash content of ca. 10 wt%, yields the slurry with the highest char and ash content (27 wt% and 11 wt%). This slurry would contain about 18 wt% of water and have a higher heating value above 16 MJ/kg. Scrap wood yields the slurry with the highest HHV-value (above 20 MJ/kg) due to low ash and water content. For moist feedstock, water contents of slurries increases, whereas its solid content and HHV decreases. Thus, the range of heating values is between 18 MJ/kg and 14 MJ/kg, water content 25-31 wt% and solid content 15-25 wt%.

The objective of KIT work in Task 2.3 was to develop procedures for preparation, handling, storage and transport of energy carriers from the conversion of biomass via fast pyrolysis. The energy carrier first of all shall be suitable for gasification and synthesis according to the bioliq concept. Besides this reference pathway, the goal is to have a pyrolysis process with products that enable flexible use in form of different energy carriers for further energetic and material applications, generating a value addition and helping to introduce the technology to the market.

The approach of the investigations done within task 2.3 of the project started with the characterization of the products as received from the pyrolysis project. The focus on the utilization of these products in form of suitable energy carriers for gasification induced the intensified investigations on biosyncrudes (slurries/pastes).

First of all, investigations on the mixing process of slurries were accomplished. The main results, which can be concluded from this work, are the findings of the most influencing parameters to optimize the slurry concerning heating value and pumpability. It can be concluded, that the porosity and the structural shape of the different char powders are the most important parameters, as they significantly impact the viscosities of the slurries.

When dealing with slurries, one crucial question is the one of their suitability, i.e. their stability as well as the energy demand for storage, transport and further processing.

Concerning sedimentation, the most important parameters are the viscosity of the liquid phase and the concentration of solid particles. In general, with decreasing viscosity of the liquid phase, the settling potential is increasing and with increasing solid concentration, the settling potential is decreasing. Additional, the solid concentration is depending on the ash content and the porosity of the used char. Basically, solid concentrations used for the bioliq process are relatively high. As a result, the particle size has a secondary importance, because with increasing solid concentration, the various settling velocities of particles changed to a consistent swarm settling velocity. Horizontal impulses – simulating motion during a road or rail transport – lead to a particle settling which is more continuous over time. From this, a separation of the liquid phase is delayed or even prevented.

Energy carriers that are to be transported from decentral pyrolysis units shall still be processible at the point of application, e.g. at a central gasifier. Solid sediments in vessels or tank wagons can lead to serious problems and down times in the process chain.

Regarding to a minimum of energy consumption for avoiding solid sediments in the biosyncrude, two possibilities are being taken into account: either the bio-slurry is continuously slowly stirred, or sedimentation is prevented by short-time stirring followed by an as-long-as-possible resting interval. It could be shown that it is completely sufficient to stir a slurry every 8 hours, until the power consumption doesn’t change. When the stirring processes are scaled up, the needed peak for re-stirring is expected to increase disproportionally high. But the energy consumption of (re-) stirring slurries batch-wise is still magnitudes smaller than the continuously stirring for keeping the slurries homogeneous.

Energy carriers with an even higher solids-to-liquids ratio need another kind of mixing device due to the more viscous nature of these mixtures. These pastes ideally show no sedimentation and are expected to be stored over longer periods of time without changing properties. No stirring would be needed during storage. A crack in a tank would not lead to leakage, thus the hazard potential of this form of energy carrier is lower than the one of a free-flowing slurry. For continuous preparation of mixtures with high char loads, extruders have been tested, potentially also suited to feed a gasifier to the required pressure. Advantages of extruders may be the intense mixing, conveying and the possibility of building-up high pressures suitable for the injection into a gasifier. Knowledge on process stability and further optimization of geometrical specifications of the extruders could be gathered during studies with two kinds of extruders. It could be shown, that solid concentration has the highest effect on energy consumption. An important result is that the twin screw extruder has a higher process stability compared to the single screw extruder. In the twin screw extruder, the screws lead to forced mixing and a highly homogeneous product quality can be achieved at solid contents of 60 wt.-% char. The general feasibility of extrusion processes for the production of char-condensate-pastes could be shown and should be followed-up by further research.

As the research on mixing, stirring and sedimentation behaviour of slurries showed that the physical properties of biomass chars play a crucial role, special regard was given to the geometry/shape, size distribution and porosity of chars.

A safe and environmentally secure handling and transport of energy carriers must be given for their introduction into the market. Flammability is an important criterion for the evaluation of safety hazards and design of adequate procedures and equipment during handling and transport. As a suitable measure for the flammability, the flash point can be considered. Hence, flash point experiments were done for different pyrolysis condensates.
From the study it can be concluded that although flammable vapors are accumulated above the pyrolysis oils, due to the high water content these pyrolysis liquids are incapable of sustaining combustion and can thus be classified as non flammable but combustible liquids.

Catalytic Pyrolysis (CERTH)

The objective of this study was to summarize the optimization results of the catalytic pyrolysis pathway towards production of an intermediate bioenergy carrier (catalytic bio-oil) that has a maximum product yield related to the biomass feed capacity with a minimum oxygen content. This bioenergy carrier can be used for the production of transportation fuels in an existing refinery infrastructure. The optimization work performed in this study aimed at the optimized catalytic materials, feedstock types and process operating conditions. The entire work was carried out in collaboration with two BioBoost partners CPERI/CERTH and GRACE. GRACE performed the catalyst synthesis and catalyst scale up while CPERI carried out the catalyst prescreening and the process optimization studies on pilot scale.

Fifteen new catalytic materials were synthesized by GRACE and tested at CPERI on bench scale. From this pre-screening study the five best catalysts were selected and scaled up at GRACE in sufficient amounts for pilot scale testing. The new catalysts and five commercially available catalysts were tested in the pilot plant after a steam deactivation procedure. It was concluded that the best BioBoost catalyst performs better than the state of the art commercial catalyst producing about 1-2%wt more oil at the same oxygen yield. This result was fully validated using the other BioBoost feedstocks. It was concluded that this catalyst is an optimum catalyst for this process. Regarding feedstock optimization the woody biomass is the best followed by the energy crop (china grass-Miscanthus) and the agricultural residue (wheat straw). As best feedstock and catalyst we are considering those that produce a higher yield of the bioenergy carrier at the same oxygen content. Regarding process optimization studies the catalyst to biomass ratio (C/B) plays a significant role since with excess catalyst the energy carrier is decomposed and the yield is descreasing. The pilot plant runs satisfactorily with C/B ratios at the range of 12-20 at the 500 °C pyrolysis temperature. It was also proved in this study that the catalyst deactivation plays an important role on the catalyst performance. Both hydrothermal deactivation and ash metal poisoning have a strong detrimental effect on catalyst stability and performance. This is of major importance for follow up studies.

From the entire work performed in this deliverable sufficient amounts of bioenergy carrier were produced from the various catalysts and feedstocks and were fully characterized using routine and advanced characterization methods. Large amounts of this carrier were given to partners in other workpackages of BioBoost for further downstream upgrading processes. The characterization studies showed that this bioenergy carrier (CPO), produced from this pathway has significant advances regarding its much lower oxygen and less organic acid content and the higher stability while it is also a source of useful chemicals like phenols. In terms of stability, the CPOs showed minimum corrosiveness, according to the copper corrosion test, even after 27 months storage. The high heating value and the total acid number value were stable but the aqueous content showed little variation, due to gradual phase separation over time. The important properties for storage and transport are density and viscosity, as they determine the pumping process. It appears that density shows slight increase after 12 months of storage, however, the viscosity slightly increases within the first 18 months and afterwards shows little variation. The results of the accelerated aging tests are in good accordance with those acquired after actual long term storage. Overall, a CPO has been produced that can be used as bio-crude in a refinery for further upgrading. The storage of the CPO at low temperatures is preferable to long term exposure at higher than room temperature, in order to avoid significant phase separation and side reactions. Normal storage containers as those used for conventional fuels can be used, since the CPO is not corrosive. Therefore, handling procedures of CPO could be the same as those employed for the conventional fuels like diesel or gasoline.

Hydrothermal Carbonization (AVA-CO2)

Separation of HTC coal from wet phase

AVA-CO2 Forschung GmbH tested two technologies for dewatering of HTC slurry:

- nano filtration (NF)
- membrane bio reactor (MBR)

For the NF tests, a modified filtration plant from OSMO Membrane Systems was used. The membranes used were made out of a polyamid-composite with a membrane filter surface of 7.5 m^2.

The first pilot test could prove the performance and process stability of nanofiltration. Against our expectation, there was a high amount of slowly degrading DOC matter in the permeate. Tests carried out with different dilution rates suggest a constant elimination rate of the organic load.

The quality of the permeate depends on the process water load and the membrane used in the nanofiltration plant. Therefore the test was repeated with a different membrane. With a high level of retention for middle sized molecules, the more difficult degrading DOC matter should be better retained by this membrane. Also the batch recipe was adjusted to reduce the loading of the process water.

The membrane bio reactor (MBR) used for this test is part of a mobile containerized waste water treatment plant of EnviroChemie. It consists of a biological cleaning part with membrane filtration an active coal filter for post treatment and a reverse osmosis plant with an expansion tank for in- and outflow. The description focusses only on the MBR tests.

Based on the 2 test scenarios, the following conclusions can be made.

Nanofiltration

- The performance of the membrane largely depends on the biomasses used for the HTC reaction and the catalyst. Modifying the operation process, membrane surface and minimal cleaning cycles can be optimized.
- A combination of different types of membranes seems to be the solution of choice to balance process performance and permeate quality. Surface needed and cleaning cycles can be reduced and operating costs are minimal.

Aerobic Waste Water Treatment

- The best removal results of the HTC permeate can be attributed to the high density of acetic acid as batch catalyst. Use of other catalysts leads to results which are a little worse, but in any case DOC in permeate is eliminated to more than 90% after 48h.
- Results show, that the required levels or purity can be reached without a MBR pre-process. It is possible that there are use cases, where this might be of importance, but generally speaking it is

not required, even for permeates out of sewage sludge. Tests showed that NF works very well and fulfill the legal requirements. The NF plant used is flexible and has a long membrane service life, which leads to low operation costs.

Storage and Handling Requirements

3 concepts for storage and logistics were elaborated taking into account particle size, humidity and safety regulations.

Determining factors are particle size and humidity, because they are defined by the use cases. As for safety requirements, only German safety requirements are taken into account. They might differ in other countries.

Tests proved, that from a storage point of view, dry pellets or chunks can be recommended, because they keep pourability even on big scale. Therefore, no forced transportation is required (screw conveyor or a shaker), molding is unlikely to happen. HTC coal in dust form also is immune against molding, even if stored in an open barrel. But storing and handling requires explosion control, which raises costs. Cementing might happen, which reduces pourability.

AVA-CO2 does not recommend storing of wet biocoal. It will mold and cement in all forms.

These recommendations are based on storage and logistics considerations. The form of the biocoal is also determined by the use case (burning plant used and feeding technologies).

Inertion cannot be recommended for large scale storage, because it is too expensive and requires tight bunkers and silos, which further raises costs.

AVA-CO2 strongly recommends drying of coal in all forms (dust, pellets, chunks) and short term usage to avoid the problems stated. With short term we mean a period of several days of up to several weeks.

For drying the wet coal, so called convective trying technologies have been tested. HTC coal is very temperature sensitive, the self ignition point being at about 100 °C. Therefore only temperatures between 20 and 80 °C have been used. Six technologies have been tested and compared with respect to drying performance, throughput and energy consumption. Data are not perfectly comparable, because some devices used, did not provide enough data collection. The advantages and disadvantages of all technologies have been analyzed and evaluated.

Therefore, there is no clear recommendation. It depends largely on specific use cases, the biomasses carbonized and their further treatment after drying.

Within the scope of BioBoost, where organic municipal waste and brewery spent grains are the most promising biomasses for HTC, mill drying is recommended. However, if an HTC plant is co-located with some industry plant (for ex. a brewery), things might change. Therefore, the project specific masterplan defines the parameters for the drying technology to choose.

Safety requirements for HTC coal have been analyzed and stated together with Wilhelm-Jost-Institut, Germany. Tests were done with pellets, dust and humid pressed cakes. Based on self ignition tests, HTC coal can be transported in barrels up to 450 l. It is classified for transportation of hazardous goods in subclass 4.2, packaging group II for HTC coal in the form of dust.

Detailed description of each section is given in Appendices A, B and C, respectively, for KIT, CERTH and AVA-CO2.

APPENDIX A
THERMAL PYROLYSIS
(KIT)

Report

A.1 INTRODUCTION

The objectives of the KIT work in WP2 of BioBoost was to optimize the technical setup and operating conditions of facilities for fast pyrolysis of dry biomass feedstock towards an energy carrier suitable for gasification and synthesis according to the bioliq® concept as well as to develop procedures for preparation, handling, storage and transport of this energy carrier. Besides these reference pathways, the goal was to have a pyrolysis process with products that enable flexible use in form of different energy carriers for alternative energetic and material applications, generating a value addition and helping to introduce the technology to the market.

A.2 EXPERIMENTAL FACILITIES FOR FAST PYROLYSIS OF BIOMASS

At KIT plants for the fast pyrolysis of biogenic residues exist on lab-, miniplant and pilot scale. Both the miniplant (10 kg h^{-1} biomass feed) – in the following referred to as process demonstration unit (PDU) – and the bioliq® pilot scale unit (500 kg h^{-1} biomass feed) make use of a twin screw mixer reactor.

In the original design of the PDU, solid product was separated in a first condensation step together with pyrolysis oil and water. In the framework of the bioliq®-concept, this is a reasonable procedure as solid and liquid products shall be fed together to an entrained flow gasifier. A second condensation step followed, yielding an aqueous condensate, consisting mainly of water loaded with organic compounds. However, for applications beyond gasification such as combustion or the extraction of valuable components, this way of product recovery is unfavorable. As a consequence, the bioliq® pilot plant (500 kg h^{-1} biomass) was constructed with a different product recovery, comprising a separation of solid particles from the hot product vapors in a cyclone followed by a two-step condensation of the vapors. In this way, a stable but viscous organic condensate with low solid and water content on the one hand, and a water-rich aqueous condensate on the other hand, can be achieved. The solids are obtained as virtually tar-free pyrolysis char particles.

In order to be able to improve and further develop the pyrolysis and product recovery process on a smaller scale, the PDU was retrofitted within BioBoost and now makes use of the optimized procedure for product recovery of the bioliq® pilot plant: Recovery of separate product fractions, which allow for a flexible use in different applications. In this way, open questions and parameter studies can be investigated more efficiently and tools for the scale-up of pyrolysis plants can be developed. The reconstruction of the PDU furthermore allows a direct comparison of the two variants of product recovery. Fig. A.1 shows a picture of the current PDU (10 kg h^{-1} biomass). Fig. A.2 shows the flow sheet of the first part of the process demonstration unit, comprising biomass storage and feeding system to the twin screw mixer reactor as well as heat carrier loop consisting of a bucket elevator, screw conveyors and a heat exchanger.

The recovery of products before and after reconstruction is shown in the flow chart of Fig. A.3. ‘Version I’ displays the former product recovery option as it was before, ‘Version II’ after modification as it is at the present time. In Version I, solids were recovered together with liquid condensate in condenser 1 in a single step at 60-70 °C, resulting in char crumbs soaked with condensates (referred to as “crumby char”). In a second condenser followed by an electrostatic precipitator, at 20-40 °C an aqueous condensate was obtained. Gases and remaining volatile compounds were discharged with a blower. In the following text, with the designation condenser 2 always the electrostatic precipitator is included in the case of Version I. In Version II, pyrolysis char powder is separated in dry state at reactor temperature in two subsequent heated cyclones. The remaining hot vapors and gases are then rapidly cooled at 80-90 °C in a quench cooler and transferred to a condensation column. The following processes are the same as in the former Version I: Aqueous condensate is recovered at 20-40 °C in condenser 2 and pyrolysis gases are sucked off with a fan.

Figure A.1: Retrofitted process demonstration plant (10 kg h^{-1}) located in the test center at the Institute of Catalysis Research and Technology at KIT

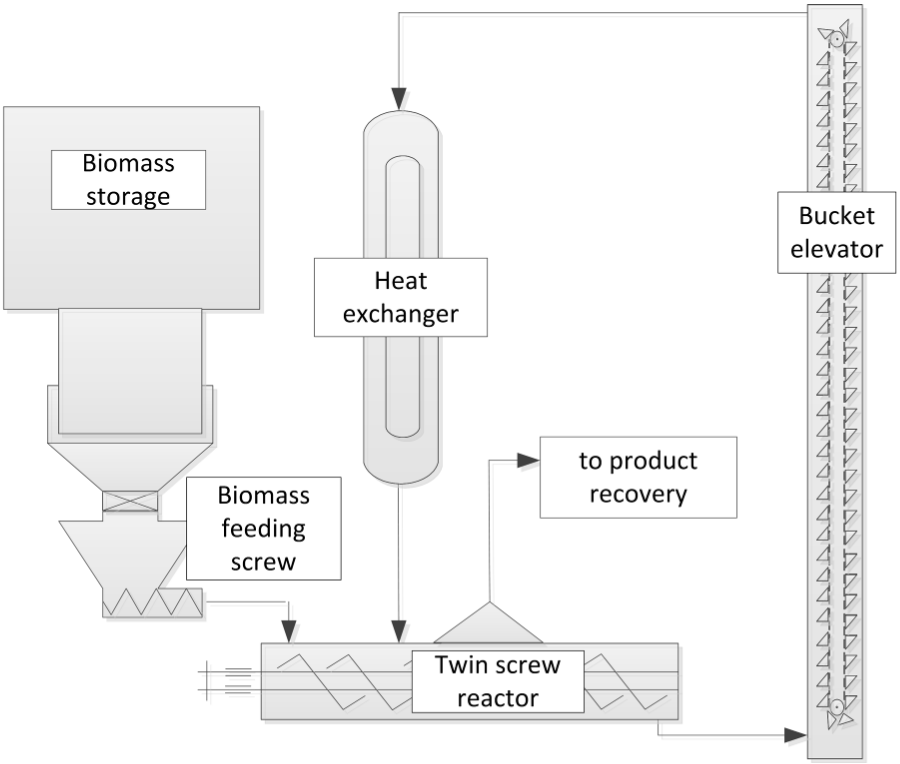

Figure A.2: Reactor and heat carrier loop

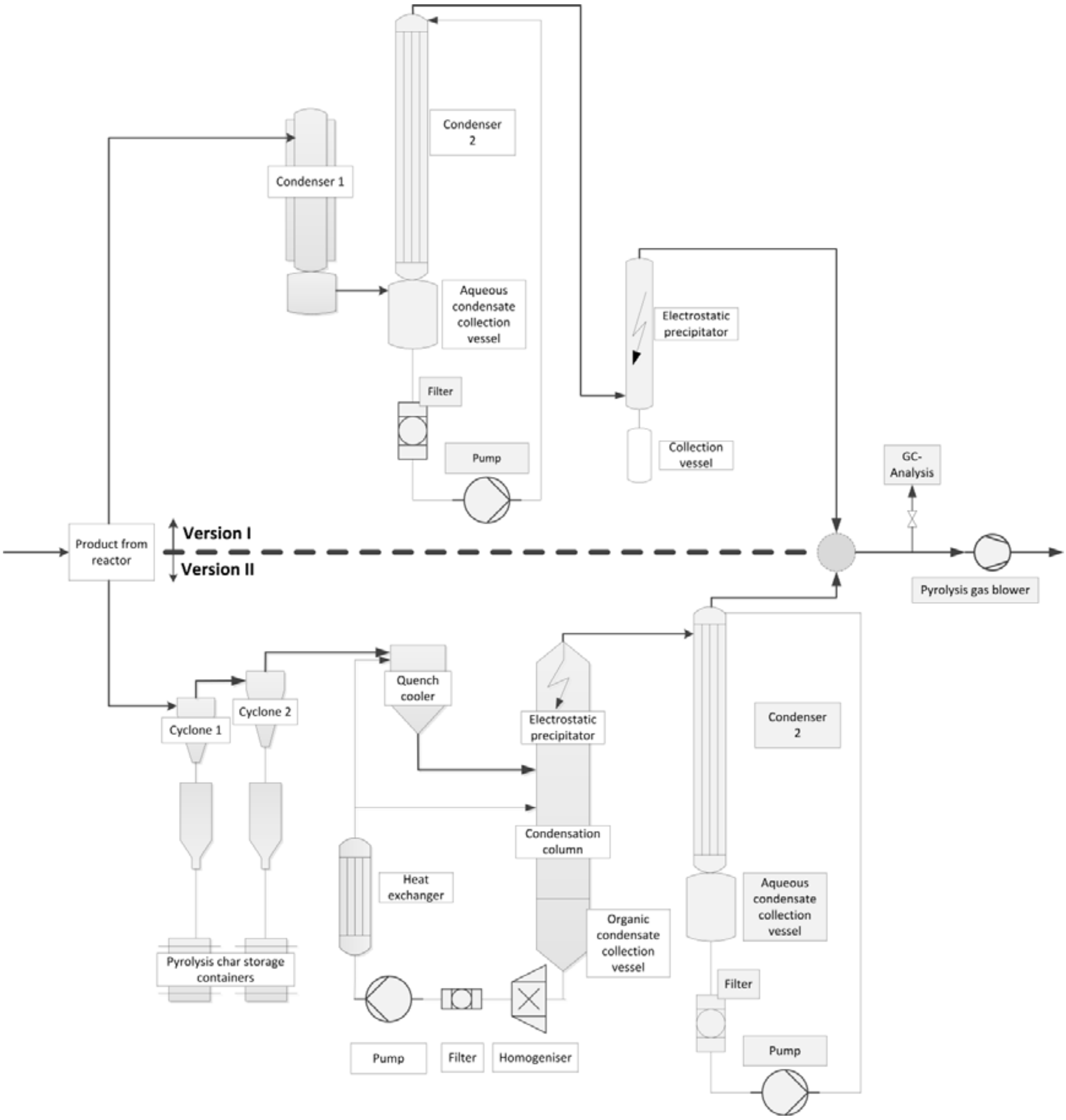

Figure A.3: Comparison of the two variants of product recovery

The figure below (Fig. A.4) shows the three types of products recovered with the enhanced setup of Version II of the PDU.

Figure A.4: Products received with Version II of the PDU;
Left: Dry char; Mid: Organic condensate; Right: Aqueous condensate

Pyrolysis experiments have been conducted with three types of biomass: wheat straw, miscanthus and scrap wood. The results from the mass, carbon and energy balances lead to the conclusion, that during the recovery of solids and condensates in a single step as in the former setup of the PDU, follow-up reactions occur producing further solids and gases.

A.3 ASSESSMENT OF THE PRODUCT RECOVERY OPTIONS INVESTIGATED

Both strategies of product recovery at PDU scale worked technically well. A qualitative assessment of the two variants is shown in Table A.1. The separation of wet char crumbs shows several advantages compared to the separation of dry char powder, especially in relation to safety aspects. Opposite to this, a higher flexibility for the utilization of the pyrolysis products is provided in case of a separate recovery of the products. Another advantage is that the organic condensate as gained in the modified PDU and bioliq®-pilot plant is flowable and pumpable, i.e. to handle with standard equipment and less effort than the sticky char crumbs produced in the former setup.

Table A.1: Assessment of the product recovery options investigated

	Version I ‘char crumbs’	**Version II ‘dry char and organic condensate’**
Safety of product handling	+	-
Flexibility in the adjustment of condensation temperatures	+	o
Flowability of products	-	+
Product flexibility (respective processing/utilization)	--	++
Complexity of plant setup	o	-
Scale-Up	o	+

Despite the successful operation of the separation of char crumbs at PDU scale according to the former product recovery procedure and the fact that tar/pyrolysis oil and char as well as mixtures of these fractions are suitable as feed for gasification, the separate product recovery as utilized in the modified PDU and the pilot plant seems to be the better option. Besides an expected better scalability, the product fractions can be mixed more flexibly to a slurry and thus can be adjusted to the needs and specifications of the gasifier, considered as fast pyrolysis reference utilization pathway in the assessment (WP 4 and 6). Furthermore, the availability of separate product fractions as char, organic and aqueous condensates creates an additional value by alternative utilization, as investigated in work package WP5 of BioBoost.

The yield of slurries is practically the same for all 3 types of biomass due to the similar yields of gases during pyrolysis. From 1 kg of biomass on a water free basis, between 0.75 to 0.8 kg of slurry can be derived. However, properties vary relatively strong, especially in terms of solid and therewith ash content. Wheat straw, having an average ash content of ca. 10 wt%, yields the slurry with the highest char and ash content (27 wt% and 11 wt%). This slurry would contain about 18 wt% of reaction water and have a higher heating value above 16 MJ/kg. Scrap wood yields the slurry with the highest HHV-value (above 20 MJ/kg) due to low ash and water content. For moist feedstock, the water content of slurries increases, whereas its solid content and HHV decreases. Thus, the range of heating values is between 18 MJ/kg and 14 MJ/kg, water content 25-31 wt% and solid content 15-25 wt%.

A.4 PREPARATION, HANDLING, STORAGE AND TRANSPORT PROCEDURES OF ENERGY CARRIERS FROM FAST PYROLYSIS OF BIOMASS

The approach of these investigations started with the characterization of the products as received from the pyrolysis process. The focus on the utilization of these products in form of suitable energy carriers for gasification induced the intensified investigations on biosyncrudes (slurries/pastes). First of all, investigations on the mixing process of slurries were accomplished. The main results, which can be concluded from this work, are the findings of the most influencing parameters to optimize the slurry concerning heating value and pumpability. It can be concluded, that the porosity and the structural shape of the different char powders are the most important parameters, as they significantly impact the viscosities of the slurries.

When dealing with slurries, one crucial question is on their suitability, i.e. their stability as well as the energy demand for storage, transport and further processing.

Concerning sedimentation, the most important parameters are the viscosity of the liquid phase and the concentration of solid particles. In general, with decreasing viscosity of the liquid phase, the settling potential is increasing and with increasing solid concentration, the settling potential is decreasing. Additionally, the solid concentration is depending on the ash content and the porosity of the used char. Basically, solid concentrations used for the bioliq® process are relatively high. As a result, the particle size has a secondary importance, because with increasing solid concentration, the various settling velocities of particles changed to a consistent swarm settling velocity. Horizontal impulses – simulating motion during a road or rail transport – lead to a particle settling which is more continuous over time. From this, a separation of the liquid phase is delayed or even prevented.

Energy carriers that have to be transported from decentralized pyrolysis units shall still be processible at the site of application, e.g. at a central gasifier. Solid sediments in vessels or tank wagons can lead to serious problems and down times in the process chain, and therefore have to be avoided at any time.

Regarding to a minimum of energy consumption for avoiding solid sediments in the biosyncrude, two possibilities are being taken into account: either the slurry is continuously, slowly stirred, or sedimentation is prevented by short-time stirring followed by an as-long-as-possible resting interval. It could be shown that it is completely sufficient to stir a slurry every 8 hours, until the power consumption doesn’t change. When the stirring processes are scaled up, the needed peak for re-stirring is expected to increase disproportionally high. But the energy consumption of (re-) stirring slurries batch-wise is still magnitudes smaller than the continuous stirring for keeping the slurries homogeneous.

Energy carriers with an even higher solids-to-liquids ratio need another kind of mixing device due to the more viscous nature of these mixtures. These pastes ideally show no sedimentation and are expected to be stored over longer periods of time without changing properties. No stirring would be needed during storage. A crack in a tank would not lead to leakage, thus the hazard potential of this form of energy carrier is lower than the one of a free-flowing slurry. For continuous preparation of mixtures with high char loads, extruders have been tested, potentially also suited to feed a gasifier to the required pressure. Advantages of extruders may be the intense mixing, conveying and the possibility of building-up high pressures suitable for the injection into a gasifier. Knowledge on process stability and further optimization of geometrical specifications of the extruders could be gathered during studies with two kinds of extruders. It could be shown, that solid concentration has the highest effect on energy consumption. An important result is that the twin screw extruder has a higher process stability compared to the single screw extruder. In the twin screw extruder, the screws lead to forced mixing and a highly homogeneous product quality can be achieved at solid contents of 60 wt.% char. The general feasibility of extrusion processes for the production of char-condensate-pastes could be shown and should be followed-up by further research.

As the research on mixing, stirring and sedimentation behaviour of slurries showed that the physical properties of biomass chars play a crucial role, special regard was given to the geometry/shape, size distribution and porosity of chars.

A safe and environmentally secure handling and transport of energy carriers must be given for their introduction into the market. Flammability is an important criterion for the evaluation of safety hazards and design of adequate procedures and equipment during handling and transport. As a suitable measure for the flammability, the flash point can be considered. Hence, flash point experiments were done for different pyrolysis condensates. From the study it can be concluded that although flammable vapors are accumulated above the pyrolysis oils, due to the high water content these pyrolysis liquids are incapable of sustaining combustion and can thus be classified as non flammable but combustible liquids.

A.5 ENERGY CARRIER USE FOR ENTRAINED FLOW GASIFICATION

At present, for the use of the energy carriers in gasification for the production of chemicals and fuels via gasification in pressurized entrained-flow gasifiers followed by synthesis, the following three forms of energy carriers are the most promising:

Organic condensate (+ ash from combustion of biomass)

Slurry of aqueous condensate + char

“All-in-one”-slurry of the three product fractions: Aqueous condensate, organic condensate, char

Fig. A.5 gives an overview on the utilization pathways for these forms of energy carriers.

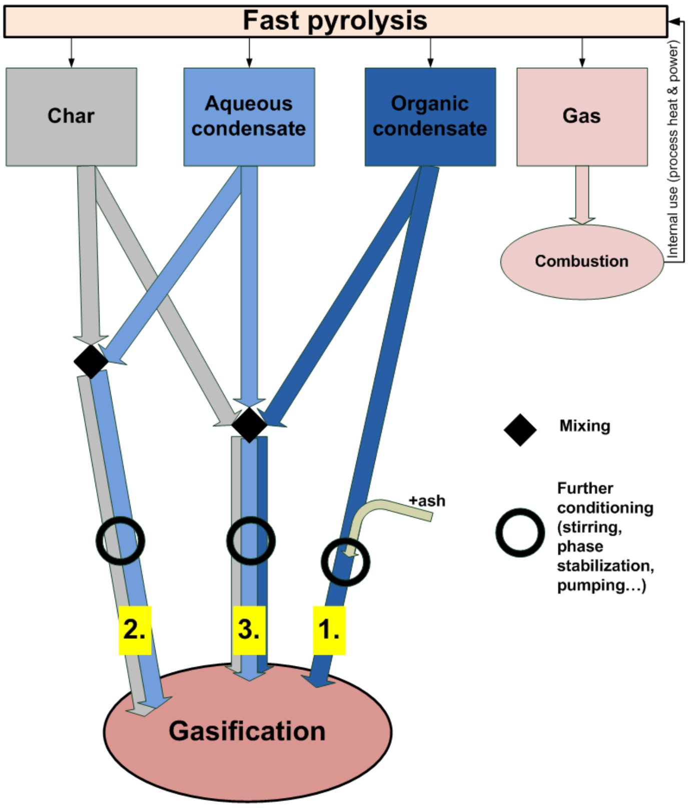

Figure A.5: Product fractions from fast pyrolysis and their utilization as energy carriers for gasification

Organic condensate (+ash).

Condensate from the first condenser has a high enough heating value, a water and solid content (particles present in the liquid due to non-sufficient separation efficiency) up to 15 wt.% of char and a viscosity that ensures its phase-stability; it still is flow- and pumpable under process conditions. For gasification in a slagging entrained-flow gasifier – as used within the bioliq® process – additional (biomass) ash and/or flux must be added to the condensate for the built-up of a protective slag layer in the gasification reactor.

Slurry of aqueous condensate + char.

The heating value of the condensate from the second condenser is too low for direct use in gasification; by adding char powder a slurry with sufficient heating value can be produced. For such a slurry with a higher heating value greater than 10 MJ/kg, the char content must be around 33 wt.% (assuming HHV_{char} = 20 MJ/kg, $HHV_{aqu.cond.}$ = 5 MJ/kg). A flow- and pumpable slurry with a tendency to sedimentation of char particles must be further conditioned after mixing. E.g., in the case of storage in vessels, the slurry needs to be hindered from sedimentation by stirrers and pumps. Depending on the content and composition of the ash of the used char, additional flux addition may still be necessary for use in a slagging entrained-flow gasifier.

Slurry of all three product fractions: Aqueous condensate, organic condensate, char.

The above described options 1. and 2. make a transport of 2 different energy carriers necessary. The option of an “all-in-one-slurry”, however, reduces complexity in terms of transport, as only one homogeneous energy carrier is dealt with. This slurry has a sufficient heating value and is pump- and flowable. However, (phase) stability for this slurry is a problem nowadays, as aqueous and organic compounds of the condensates tend to form two phases within relatively short times. This of course also depends on the type of feedstock used – woody biomass produces less water in pyrolysis than ash-rich straw – and the properties of the produced condensates. Experience shows that at water contents in the condensate 1 higher than 20 wt.%, phase separation into a light water-rich and a heavy tar-rich phase can occur. Therefore, further conditioning like addition of surfactants is necessary in order to attain a stable product. Also, the option of reducing the water content in the condensates for a better phase stability is under investigation. This may either be done by further drying the feedstock before feeding to the pyrolysis reactor or by separation of water from the condensates with help of membranes in the process or subsequently.

At this point in time, of the above described options, no. 1 and 2 can be produced and conditioned in a way that enables use in gasification. Large technical gasifiers with input capacities of several 100 MW will have several independent feed lines – for safety reasons and flexibility – so it is possible to feed one line with organic condensate (+ ash) and another one with a slurry of aqueous condensate + char (+ash). Option no. 3 is not yet feasible in a technical scale due to stability problems and further research on this topic is necessary in the future. The timeline shown in Fig. A.6 illustrates the advancement in the utilization of different feeds in the pilot gasifier of the bioliq® process.

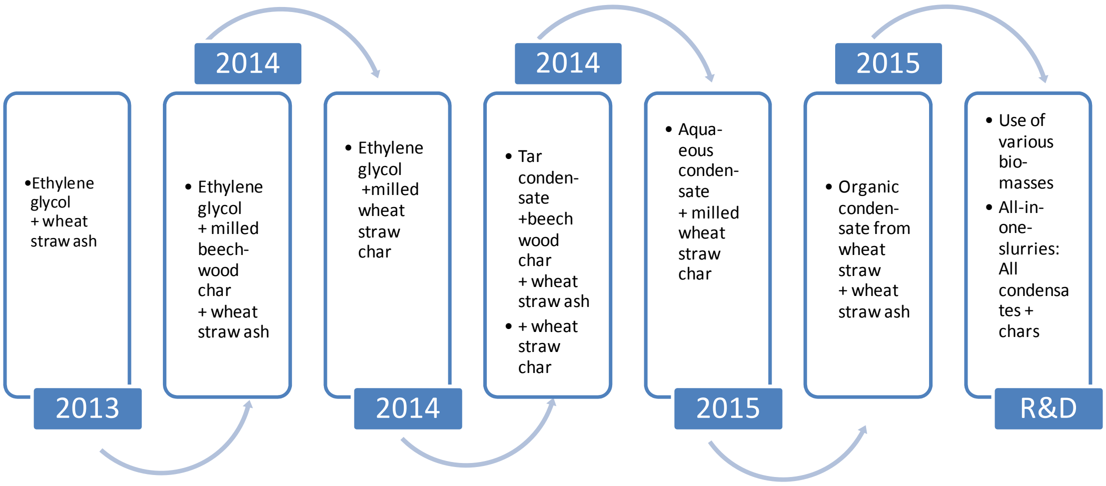

Figure A.6: Development of utilization of energy carriers in the bioliq® pilot gasifier

A.6 CONCLUSIONS

Fast pyrolysis offers a broad spectrum of energy carriers that can not only be used in gasification – the reference pathway followed at KIT’s bioliq® process – but also for various applications in heat and power or substantial use. The results obtained during the BioBoost project are very helpful for the progressions on applicability of pyrolysis products for gasification and their market implementation as energy carriers also beyond gasification. Biosyncrude – either as flowable slurry or non-flowable paste – can be customized according to the specifications for the following applications in a wide range. However, the knowledge gained during this project now needs to be exploited in coming research activities, as there are still wide gaps in the understanding of processes during production and handling of the energy carriers.

APPENDIX B
CATALYTIC PYROLYSIS (CERTH)

Report

B.1 INTRODUCTION

The objective of this deliverable was to summarize the work performed in WP2 for the optimization of catalytic pyrolysis pathway towards production of an intermediate bioenergy carrier (catalytic bio-oil) that has the maximum yield (on a biomass feed basis) with the minimum oxygen content. As it was proved in WP5 by NESTE this bioenergy carrier can be used for the production of transportation fuels within an existing refinery infrastructure. The optimization work for this pathway concerns optimum catalytic materials, feedstock types and process operating conditions. The entire work was carried out in collaboration with two BioBoost partners CPERI/CERTH and Grace. Grace performed the catalyst synthesis and catalyst scale up while CPERI carried out the catalyst prescreening and the process optimization studies on bench and pilot scale. Technical parts of the work in this deliverable have been already described in details in two other deliverables: Del.2.5 and Del.2.9. For this reason in the following some of the work refers to the previous already submitted deliverables. In the first part of the current deliverable we described the work performed towards optimization of catalysts, feedstocks and operating conditions of the catalytic pyrolysis for the production of a high quality catalytic pyrolysis oil (CPO) while in the second part we are describing the characterization of the CPO along with optimum options for storage, handling and transport of the CPO.

B.2 EXPERIMENTAL

B.2.1 Biomass Feeds

As it was described in Del.2.1 three types of biomass were used in this study: a woody biomass (beech wood with the commercial name Lignocel), an agricultural residue (wheat straw supplied from KIT) and an energy crop (Mischanthus). The biomass feed characterization is presented in Table B.1. From Table B.1 it is clear that there is a difference in the ash content of the feeds. The Lignocel contains a very low ash content while the straw a high value (about 4.5%wt). The energy crop has an ash content between the other two feedstocks. In the ash of the straw and Mischanthus the potassium (K) dominates while calcium (Ca) and magnesium (Mg) are also in high concentrations. Regarding moisture content the two biomass feeds (Lignocel and straw) have similar values (around 8%wt) while the energy crop has a lower value (5.3%wt). Before the use of the three biomass feeds in the units a pretreatment procedure was performed in order to obtain them in the appropriate particle size for feeding into the CPERI pilot plant pyrolysis units (more details in Del.2.5).

B.2.2 Catalytic materials

Fifteen (15) novel catalysts were synthesized by GRACE and sent to CERTH for evaluation. These catalysts were of the following general types: i) Six (6) catalysts with different types of matrices, ii) Three (3) catalysts with Pt doped alumina (different Pt loadings), iii) Six (6) catalysts with different types of ZSM-5 materials. Moreover, four (4) commercially available fresh FCC type catalysts were also provided by GRACE plus one (1) commercial ZSM-5 based catalyst: One (1) high ZSA catalyst, One (1) high MSA catalyst, One (1) high Activity catalyst, One (1) Silica Sol catalyst, One (1) ZSM-5 based commercially available sample.

The fresh properties of the new and the commercial catalyst samples were presented in Del.2.5.

B.2.3 Experimental units used in BioBoost

The biomass pyrolysis experiments for catalyst pre-screening were performed on a bench scale fixed bed pyrolysis reactor made of stainless steel 316. The reactor is heated by a three zone furnace and is purged with nitrogen to ensure an oxygen-free atmosphere and to carry the pyrolysis vapors through the catalyst. Full description of this experimental unit along with the details on the analysis of the products produced from this unit is given in Del.2.5.

The process optimization tests and the scaled up catalyst screening tests were carried out in the biomass catalytic pyrolysis pilot plant unit presented in Fig. B.1. This unit employs circulating fluidized bed

(CFB) pyrolysis technology and works in a capacity range of about 1-1.5 kg/hr. This pilot plant operates in a fully circulating catalyst mode with continuous catalyst regeneration. It was used for catalyst evaluation studies and led to the production of sufficient quantities of bio-oil for full characterization. The process unit can be divided into five unique sections: biomass feed, catalyst feed, reactor/mixer, product stripper - solid/vapor separation and liquid product recovery. Full description of this pilot plant along with details on the analyticals of the products is given in Del.2.5.

For the hydrothermal deactivation of all fresh catalysts before testing in the pilot plant a pilot plant steamer unit was used. The unit consists of a quartz fluid bed reactor that can hold a catalyst inventory of 6 kg along with the appropriate feed systems for introduction of vapor and nitrogen into the catalyst. The reactor is heated by a three zone furnace.

B.2.4 Physicochemical characterization of the CPO

The CPoils produced from the pilot plant were fully characterized by elemental analysis and analysis of the density, viscosity, total acid number, water content and copper corrosion abilities. The standard and modified methods applied for the physicochemical characterization of the CPO and the accelerated aging procedures are described in details in Del.2.9.2. For the detailed chemical characterization of the CPOs a two-dimensional gas chromatography technique was applied. This is an advanced separation technique that uses two columns of different polarity, connected sequentially, thereby allowing separation of the compounds both due to their boiling point and polarity. This technique was applied in connection to a time-of-flight mass spectrometer that allows the positive identification of many unknown compounds at a wide range of molecular weights. The GCxGC-ToFMS was used for the qualitative and quantitative analysis of the bio-oils. The qualitative identification of the compounds was based mainly on the match of the spectra with those of the official library NIST05, therefore S/N at 50 and similarity value at 700 were set as minimum identification criteria. For the quantitative analysis, a standard solution consisting of 39 compounds, in particular 11 aromatic hydrocarbons, 5 PAHs, 1 aliphatic hydrocarbon, 4 furanoics, 4 carbonyl compounds (including cyclopentanones and aromatic aldehydes), 12 phenolic compounds and 2 anisoles (considered as ethers), was prepared and was used for the recording of the relevant retention times as additional identification criteria. Details of sample pretreatment, on the conditions applied on the apparatus (columns, internal standard etc.) and on the developed quantitative method are given in Del.2.9.2.

B.3 EXPERIMENTAL RESULTS AND DISCUSSION

B.3.1 Catalyst selection and scale up

The 15 catalysts synthesized by Grace and the 5 commercially available samples were evaluated on the small scale pyrolysis unit. It was proved in CPERI that the ranking of catalysts in the bench scale unit is consistent with that in the pilot plant (K.Kalogiannis, S.Stefanidis, S.Voutetakis and A.Lappas, AIChE meeting, 7-12 Nov., 2010, Salt Lake City USA). All these catalysts were tested as fresh. From these experiments full mass balances were performed and a complete characterization of the products was carried out and presented in Del.2.5 (along with results from thermal pyrolysis using an inert material-silica sand). It is known from the literature that in comparison to thermal pyrolysis the presence of catalyst causes a reduction in the yield of the organic oil with a corresponding increase in the water, gas and coke production. This is fully confirmed in this study. However, on the other side, the quality of the produced bio-oil is better since it contains less oxygenates and thus, overall less oxygen content. For this reason Fig. B.2 presents the O_2 in total organic Oil vs. total organic Oil yield (%wt on dry biomass) for all catalysts tested for catalyst pre-screening purposes. This organic oil is the combination of total organics from both aqueous and organic phases.

It is clear that catalysts producing more organic yield with the less oxygen content are the best catalysts for this process. From Fig. B.2 it seems that there are catalyst families that are in the same straight line. These catalysts have essentially the same selectivity for the oil yield but they differ in their activities (deoxygenation). For this process the catalyst families (in the same line) that are located in the right and lower part of the plot are better since for the same oil yield they produce an oil that has lower oxygen content. These catalysts achieve better deoxygenation but at the same liquid yield. From Fig. B.2 it is concluded that matrix catalysts M4, M2 and M5 are in the same line and they are the worst catalysts of all. M6 and M3 are in a different line and are better matrix catalysts while the M1 is the best matrix catalyst of all. ZSM-5 based catalysts are in the same line and they are by far the best catalysts for this process. Among the ZSM-5 based catalysts ZSM-5 alternative matrix, ZSM-5 w/matrix, ZSM5-1 and ZSM5-3 are the best catalysts. From the three Pt based catalysts it appears that although these catalysts are not the best for yield production it is possible that the Pt plays a role in deoxygenation. The high Pt catalyst presents a better deoxygenation compared to low Pt catalyst. Extensive studies in CERTH have shown that the effect of catalyst properties on biooil deoxygenation depends on the acidity and type of acidity of ZSM-5 based catalysts. In general the more acidic ZSM-5 causes more deoxygenation (higher production of CO, CO_2 and H_2O). The same is also valid for the aluminosilicates materials (like the matrices tested in the project). However, it seems that it is not only the acidity but also the porosity that plays a significant role in the performance of the catalyst. The porosity affects the coke production from the process. It is in general difficult to find specific correlations that relate catalyst properties with product yield and distribution in catalytic biomass pyrolysis. Based on the results from the previous paragraph from the 15 novel catalysts synthesized by Grace, five proved to be the best from the pre-screening studies. These catalysts were the following:

- ZSM-5 alternative matrix (named in this report as ZSM-5 alternative matrix)
- ZSM-5 with matrix (named in this report as ZSM-5 w/matrix)
- ZSM-5 based FCC catalyst No.3 (named in this report as ZSM-5 based FCC)
- Alumina matrix (named in this report as Alumina matrix)
- Alumina matrix CP3 (named in this report as Alumina matrix CP3)

Grace scaled up these catalysts at 20 kg level. The manufacturing scale up process of pyrolysis catalysts contains a particle-shaping unit operation to produce particles that can be fluidized in the pyrolysis pilot plant. The developed catalyst particles have been produced by a spray drying process. In Del.2.5 full description of the methodology applied in GRACE for the scaling up of the catalysts is presented. The scaled up catalysts were sent as fresh to CPERI/CERTH for evaluation on pilot scale. The fresh properties of these 5 catalysts are given in Table B.2.

B.3.2 Selection of a deactivation protocol

It is known that even refining catalysts are deactivated when they are used in commercial units. For this reason the catalyst testing after a deactivation procedure represents a better evaluation study compared to testing catalysts as fresh. The selection of a laboratory deactivation procedure is a complicated task and should be based on literature studies. However, catalyst deactivation under biomass pyrolysis conditions was not investigated in the literature. Based on the above and in order to examine in BioBoost if deactivation could play a role on catalyst performance in the unit we carried out a pilot plant study by testing the ZSM-5 based commercial catalyst as fresh and after two different hydrothermal deactivation severities. Specifically, the catalyst was tested on pilot scale with the following forms: i) as fresh, ii) after a mild severity (MS) hydrothermal deactivation: 788°C/12 hrs/100%steam and iii) after a high severity (HS) hydrothermal deactivation: 815°C/12 hrs/100%steam.

The hydrothermal deactivations were carried out in the pilot scale steamer reactor. The properties of the catalyst after the mild and severe deactivation protocol (presented in Del.2.5) were comparable even after the more severe deactivation protocol. However, it seems that by steaming more zeolite is destroyed and more matrix is created given overall a high total surface area compared to fresh sample. The experimental results from the testing of the three different deactivated catalysts on pilot scale and using the woody biomass are presented in Del.2.5. In Fig. B.3 we present the key plot that shows the deoxygenation achieved with the three deactivated catalysts. It is clear that deactivation has a major effect on decarbonylation/decarboxylation/dehydration reactions and thus, on the deoxygenation level. A severely deactivated catalyst can decrease at least 10% the deoxygenation level. From this work it was shown that fresh catalyst is more active resulting in higher cracking and thus lower oil. The higher the deactivation severity the less active is the catalyst. At the same C/B ratio a severe deactivated sample can produce around 6-7%wt more organic oil.

The hydrothermal deactivation study described above showed that the catalysts are affected by the hydrothermal deactivation. Based on CPERI and Grace knowledge and experience from refining catalyst deactivation technology it was decided to test all catalysts on pilot scale not as fresh but after the 1450/12/100 steaming protocol. It must be mentioned that this is also a standard protocol applied to refining catalyst deactivation.

B.3.3 Process optimization and evaluation of the commercial catalysts with the woody biomass

In the initial phase of this project CPERI performed an evaluation study using different commercially available catalysts. The objective of this study was : i) to have a base case with commercially available catalysts, ii) to compare the new BioBoost catalysts with the best commercial catalyst, iii) to investigate C/B effects on pyrolysis products, iv) to collect sufficient amount of bio-oil samples for complete characterization and for sending to other workpackages (WP3, WP5).

In this study the C/B ratio was changed independent of the pyrolysis temperature by keeping this temperature constant at 500 °C. Based on literature and previous CPERI experience this temperature is an optimum temperature for the catalytic pyrolysis process. All five commercially available catalysts were tested in this study after steam deactivation. Following steaming the catalysts were evaluated on pilot scale using the C/B ratio as the main variable at constant pyrolysis T = 500 °C. All experimental results from this study were presented in Del.2.5. Key findings are given in the current deliverable. It seems that for all catalysts the C/B ratio affects the yield of organic oil by accelerating the cracking reactions thus resulting in a lower oil yield. By increasing the C/B ratio from 10 to 25 the oil yield descreases about 7%wt. In Del.2.5 we showed that the C/B ratio does not affect the water yield (dehydration reactions), however, the higher the C/B ratio the more coke is produced. CO is more affected by increasing C/B ratio while CO_2 increases only slightly with the C/B ratio. It seems that deoxygenation reactions can occur even with lower catalyst and thus further increase in C/B ratio has no additional effect. From the pilot plant studies it was concluded that a C/B ratio of about 15 is the optimum for this process.

Regarding the evaluation of the commercially available samples (details in Del.2.5) it seems that for high oil yield the commercial ZSM-5 catalyst is the best followed by silica sol and high ZSA. The high activity and the high MSA catalysts are the worst of all giving around 15%wt less oil than the ZSM-5 catalyst. However, if we compare the catalysts regarding their selectivity to produce oil with less oxygen content (Fig. B.4) there is a clear differentiation. ZSM-5 is the best catalyst followed by high activity, silica sol and high ZSA catalyst. The worst catalyst is the high MSA. At the same oxygen content of bio-oil (for example 20%) ZSM-5 gives 15%wt more organic biooil than high MSA and 10% than all other 3 catalysts. Regarding deoxygenation activity of the three similar (to selectivity) catalysts the Silica sol is the less active followed by the high ZSA while the high activity is the most active (Fig. B.4).

B.3.4 Evaluation of the new BioBoost catalysts

All BioBoost scaled up catalysts were tested after deactivation of 788/12/100. The properties of the fresh and steamed catalysts are given in Table B.2. The results from the evaluation work of the five steamed BioBoost catalysts are presented in details in Del.2.5. Figs. B.5 & B.6 present the C/B ratio effect on oil and coke products yields from the pilot scale new catalysts evaluation studies. For comparison purposes we include in these figures the experimental results with the best commercial catalyst (ZSM-5) as it was concluded from the section 3.3. From the figures it seems that the C/B ratio effects on all products are very similar to those discussed in the section for the commercial catalysts. The C/B ratio decreases mainly the oil yield (overcracking of biooil vapors) by increasing more the coke production while its effect on water, CO, CO_2 and gases yield is not that pronounced. Fig. B.5 shows that for all catalysts the increasing C/B ratio results in a lower organic oil yield by accelerating the cracking reactions. From the ZSM-5 type catalysts, the ZSM-5 w/matrix catalyst is the most active of all (for cracking biooil vapors) followed by ZSM-5 based FCC catalyst and commercial ZSM-5 while ZSM-5 alternative matrix is the less active of all. This last catalyst gives the highest oil yield. Of course the difference in oil yield between all these catalysts is about 7%wt. Regarding the alumina type catalysts, they seem to be more active than the ZSM-5 type ones. Especially the Alumina matrix CP3 catalyst is extremely active. There are no significant differences in the yields of water, CO, CO_2 and other gases between the catalysts. However, the catalyst type affects significantly the coke yield. Fig. B.6 presents the C/B ratio effect on coke yield for all catalysts. From this figure it seems that from the ZSM-5 type catalysts, the ZSM-5 alternative matrix and ZSM-5 based FCC are the best catalysts followed by the commercial ZSM-5 while ZSM-5 w/matrix gives the highest coke yield of all. Alumina type catalysts are more coke selective than the ZSM-5 ones with Alumina matrix CP3 yielding the highest coke of all. However, if we examine the selectivity of these catalysts at the same O_2 in oil (deoxygenation) it seems that the ZSM-5 based FCC catalyst is the best although slightly better than the commercial ZSM-5 (Fig. B.7). Regarding the alumina type catalysts, it seems that the performance of Alumina matrix is similar to that of the ZSM-5 type catalysts although it is less selective to deoxygenation than the ZSM-5 materials whereas the Alumina matrix CP3 is very active achieving very low O_2 in oil values but with low oil yields.

The overall conclusion from this study is that ZSM-5 based FCC catalyst is the best catalyst among all new catalysts and moreover this catalyst is slightly higher than the best commercial catalyst (ZSM-5). At the same oil yield this new catalyst can give around 1% less oxygen content compared with the state of the art commercial catalyst. Moreover, the ZSM-5 w/matrix catalyst although not the best for selectivity is more active than all catalysts (except for Alumina matrix CP3) and with this catalyst we can achieve oxygen in oil around 14% which is a very low value. Of course with this oxygen content we sacrifice organic yield that is at the level of 20%wt (on biomass). Finally, the Alumina matrix CP3 catalyst is the most active of all achieving very low O_2 in oil (~6%) but with extremely low oil yields (at the level of 7.5%wt).

The best BioBoost catalyst and the best commercially available catalyst were tested with the agricultural residue (wheat straw) supplied by KIT. The relative ranking results were similar with those described above for woody biomass. The new BioBoost catalyst gives slightly less coke and clearly more CO and less CO_2 while the deoxygenation rate of the new catalyst is better than the commercial one producing an oil with less oxygen content. Fig. B.8 presents the oil yield vs. oxygen in oil for the two catalysts with the straw feed. From this figure it seems that with the commercial catalyst and the wheat straw we can produce an oil yield of about 25%wt with about 20% oxygen in oil. With the new BioBoost catalyst we can produce the same oil yield with about 18% oxygen in oil. It is clear that the best BioBoost catalyst is even better when a wheat straw feedstock is used compared with the woody biomass.

B.3.5 Feed evaluation studies on pilot scale

In BioBoost biomass feed effects on catalytic pyrolysis were studied on pilot scale using the three different feeds described in section 2.1. These three feeds were pyrolyzed in the pilot plant unit using the best commercially available catalyst which was steamed prior to testing according to the protocol described previously. From the experimental results of this study it seems that the different biomass types give different yields of the various pyrolysis products. Moreover, it is also concluded that the C/B ratio affects the product yields of Mischanthus and wheat straw in the same way as in the case of Lignocel (discussed in section 3.4). Regarding product yields, the pyrolysis of wheat straw gives more CO_2 yield compared to the woody biomass and Mischanthus feeds while its CO yield is between the other two feeds. This can be explained by the fact that the agricultural feed contains more carboxylate and less carbonyl groups. Coke and char are higher with Mischanthus probably due to additional catalytic activity of the (higher) ash content. For the water yield there are no significant differences between the three feeds. Oil yield from the energy crop is between the other two feeds. The same is also valid for the two individual cuts (gasoline & HCO) coming from Mischanthus. Regarding bio-oil yield and O_2 in biooil, the Lignocel feed produces the highest oil yield with the lowest O_2 content followed by Mischanthus and Straw (Fig. B.9). However, the oxygen concentration in the bio-oil of Lignocel is significantly lower. Compared to the other feeds the Lignocel gives the best quality of bio-oil (less oxygen) with only a small decrease in yield. Deoxygenation is accordingly higher for Lignocel derived bio-oil.

B.3.6 Catalyst deactivation with ash metals

As it was mentioned in section 3.2, an important question when dealing with the upgrading of biomass via catalytic pyrolysis is that of catalyst deactivation. During the process, the hydrothermal process conditions as well as high temperatures during catalyst deactivation and contaminant metals deposited on the catalyst will reduce the catalytic activity. The contaminants originating from the biomass fed to the process may be deposited on the catalyst during the pyrolysis. The main contaminants that are found in the biomass are sodium, potassium, magnesium, calcium and phosphorus. Known metals deactivation mechanisms are the blocking of the acidic, catalytically active sites by e.g. sodium, and the formation of silicates by e.g. the alkaline earth metals.

In addition to the hydrothermal deactivation studies presented in section 3.2, GRACE carried out a preliminary study in order to investigate metal poisoning effects on the catalysts. Thus, CPERI returned the retain samples of the commercial catalysts used for the initial riser tests to GRACE. The catalysts were analyzed by ICP-OES for the metals deposition during the short pilot-scale pyrolysis experiments. Based on the metals found on the retains, it was possible to make an educated guess about the metals concentration ratios for an equilibrated catalyst with longer average equilibration times, or estimated times on stream, during a commercial run. To mimic this combined deactivation effect by metals contamination and by the impact of the hydrothermal conditions, the “commercial” ZSM-5 pyrolysis catalyst has been treated with six different metals levels corresponding to 2, 10, 20, 30, 40 and 50 days on stream (Table B.3). The corresponding contaminant amounts have been impregnated on the fresh catalyst sample via spray impregnation in a turbulently fluidized bed reactor. For the impregnation, the alkaline and alkaline earth nitrates as well as ammonium phosphate have been used. The impregnated samples have been calcined in order to decompose nitrate and ammonium residues, and subsequently subjected to a steaming at 815 °C for 24 hours. Our results show that the ZSM-5 based material remains quite stable until a threshold level of the contaminant metals corresponding to about 20 days on stream. After this time the catalyst deactivates rapidly.

In order to examine the deposition rate of the metals on the catalyst the best BioBoost catalyst was studied using a long experimental run (100 hrs) in the pilot plant unit in order to investigate the degree of deactivation with the deposition of biomass metals. A series of runs took place for the study of the catalyst’s deactivation. In each test 2 kgs of woody biomass were pyrolyzed for about 4 hours each time. All tests were carried out at 500 °C. The total time of each test including catalyst circulation before biomass introduction and after the end of feeding was about 6 hours in each run. Overall 27 individual runs were completed corresponding to total biomass run time of over 100 hours. Between runs the catalyst was left in the regenerator at a temperature of 650-675 °C. During the regeneration of the catalyst when coke was burnt off, temperatures of up to 705 °C were measured. During the course of the entire deactivation run the C/B ratio varied in the range C/B=12-15. More details of the procedure are given in Del.2.7. In Fig. B.10 we present the total quantities of metals deposited on the catalyst in the course of the long run as measured by ICP versus the quantity of the treated biomass. From these results we concluded that the biomass metals are mainly deposited on the catalyst surface in an almost proportional way. Table B.4 presents the effect of catalyst deactivation on product yields. After metal deactivation the catalyst has lost activity by increasing the biooil yield however with higher oxygen content and less deoxygenation.

B.3.7 Biooil collection and characterization

From the pilot plant tests sufficient amounts of the produced biooil were sent to WP3 for work regarding phenols extraction and to WP5 for deoxygenation studies of the biooil. Table B.5 includes the properties of the biooils produced from the scaled up new BioBoost catalyst and the commercial one using the woody biomass feed (lignocel). In Table B.6 we present the effect of feedstock (lignocel vs. wheat straw) on the quality of biooil using the commercial available ZSM-5 catalyst and the ZSM-5 based FCC catalyst of BioBoost. From Table B.5 it seems that the carbon content of the CPOs produced from various catalysts is in the range of 72.4-85.4%wt. The values of hydrogen content do not vary significantly (5.2-7.4%wt), therefore the oxygen content, that is a key parameter for the quality of this EC since it reflects the degree of deoxygenation, can vary from 8 up to 22.4%wt. The CPO density is not affected by the type of catalyst and it can be considered to be 1.1g/ml while the corresponding heating values are between 29.5 and 35.1 MJ/kg. This heating value is slightly affected by the presence of small amounts of water that is not separated from the CPO. The TAN number, that is a measure of CPO acidity, varies between a low value (0.95) and 47.9 when lignocel is used as a feedstock and it seems to be mainly catalyst dependent (Table B.5) and less feedstock dependent (Table B.6). The MCRT which is a property that shows the tendency of the CPO to produce coke demonstrates values between 12.8 and 20.8 and it seems also to be more catalyst dependent rather than feedstock dependent. The study of the physicochemical properties of the CPOs produced at the pilot plant together with the oil yield produced confirmed that the best catalyst was the ZSM-5 based FCC, since it resulted in the CPO with the highest deoxygenation degree and the maximum yield. This oil presented the lowest aqueous content and TAN value and the highest HHV, while its density is sufficiently low. Compared to the commercial catalyst the ZSM-5 based FCC CPO presents lower oxygen content (at least by 3 units), significantly less TAN value (more than 10 units), and lower MCRT thereby possessing overall more favorable properties as an EC.

B.3.8 Qualitative and quantitative chromatographic analysis of catalytic pyrolysis oils

The organic phase of the CPOs produced from all studies in BioBoost was properly diluted in methanol and analysed by GCxGC-ToFMS. Full chemical characterization results are given in Del.2.9.2. The detailed quantification of two CPOs is presented in Table B.7 whereas an overall distribution of the quantified compounds is presented in Table B.8. It is clear that these oils are very rich in phenolic compounds, while they also present considerable peak density at the aromatic hydrocarbons derivatives area.

From Table B.8 it seems that the high ZSA, high MSA and high activity catalysts appear to promote the formation of phenols since phenol and cresols, are among the primary compounds, instead of aromatic compounds. On the other hand the silica sol catalyst resulted in a bio-oil rich in furfural and cyclopentanone derivatives. The ZSM-5 based catalysts result in CPoil with increased aromatic and polyaromatic hydrocarbons content while phenolic compounds are produced as well. The order of catalysts based on decreasing of hydrocarbons production is ZSM5 alternative matrix>FCC based ZSM5>ZSM5>ZSM5 w/matrix>high MSA>high activity>high ZSA>silica sol. The aromatic compounds with the highest concentration are p-xylene, toluene and 1,2,3-trimethylbenzene. Regarding the production of phenols the catalyst order is FCC based ZSM5>ZSM5 w/matrix>high MSA>high activity>ZSM5≈ZSM5 alternative matrix>high ZSA>silica sol. The phenolic compounds produced at higher concentration are phenol and cresols. The effect of the catalyst is also pronounced by the lack of methoxy-phenols, such as guaiacols and syringols, replaced by alkyl-phenols.

B.3.9 Stability, storability and handling of the catalytic pyrolysis oil

A CPoil produced in CPERI via the catalytic pyrolysis of lignocel over the ZSM-5 commercial catalyst was analysed periodically in order to assess its stability under storage in a cool room at 4 °C (Table B.9). Table B.9 presents the bio-oil properties after storage in a cool room (CR) at 4 °C, in dark for 6, 12, 18, 22, 27 months. It is observed that there is a gradual increase in viscosity which is mainly attributed to an aqueous phase separation (from visual observations). The water is dispersed in the organic phase of the catalytic biooil and is gradually separated over time, as a separate layer. The analysis showed that there is a slight increase in the CPO density the first 6 to 12 months after its production, after which it is rather stable with minor changes in its density. The heating value and the TAN are two properties that are not affected by the storage for 27 months. The elemental analysis and the copper corrosion also appear to remain constant and unaffected by the storage time.

In the same CPO we also performed two accelerated aging procedures: i) at 80 °C for 24h and ii) at 40 °C for 7 days. The recorder values for long-term storage correspond well with the predicted ones after accelerated aging. If we compare the properties of the CPO after long term storage with the results of the accelerated ageing it seems that the accelerated ageing at 40 °C for 7 days represents satisfactorily the long storage for about 18 months. The accelerated ageing at 80 °C for 24 hrs is more representative for storage of about 1 year.

In Table B.10 we present the properties of the CPOs produced from various catalysts synthesized in BioBoost and also from different feedstocks. In general we can conclude similar results with those discussed for Table B.9. The accelerated aging does not affect the HHV of the CPOs independent of the catalyst or feedstock used. Moreover, with the BioBoost catalyst density and viscosity is only slightly affected by accelerated ageing and also TAN number is only slightly increasing. Water content and flash point variations are within experimental error of the measurements; however, there might be a small loss in volatiles that may affect slightly the elemental analysis of the CPO although the differences are small.

Considerable work was carried out by NESTE and CERTH for the identification of the most important properties of the CPO in order to be suitable for handling it in refining infrastructure. These properties are:

i) CPO acidity. The acidity is important as most materials in refinery storage tanks are carbon steel which could corrode if CPO is acidic. There are some mild acids and water retained in the CPO phase which could corrode normal storage tanks depending on the conditions of storage. As we discussed in the previous paragraph there is acidity in the CPO, however, this is small and in most the cases less than about 42 mgKOH/g. For BioBoost catalyst it is almost 30 mgKOH/g. The acidity of the CPO is not affected by the storage at 4 °C for 22 months and even by keeping it at 40 °C for 7 days. There was a small increase in TAN after heating at 80 °C. From corresponding literature studies performed in deoxygenated biooils with higher TAN numbers we can conclude that there is no problem with this acidity of the CPOs. This was also validated in the present study from the copper corrosion tests discussed in the previous paragraph. In all cases copper corrosion was 1A even after accelerating ageing. This means that indeed we do not expect corrosion problems from the CPO.

ii) CPO stability. In order to pump the CPO into the refinery feed lines, the viscosity must be sufficiently low. This may require heated tanks. In addition, prior to feeding into the refinery units, the CPO must be heated up to operating temperatures. This is normally done in heat exchangers. This requires that CPO does not react or form deposits on the heat transfer surfaces. Heat transfer surfaces have been designed according to the properties of mineral oils and surface temperatures can be quite high compared to the liquid temperature itself.

From the studies performed in CERTH and discussed in previous paragraph it seems that CPO is very stable. There is a small increase in the viscosity in the first period after its production, however, this increase is very small and it is not going to affect the pumpability of the CPO. As it was mentioned this small increase is due to aqueous phase separation and some loss of light volatiles. However, it is expected that in industrial case water separation will be more effective leaving less water in the organic phase and thus, less water for further separation under storage. Moreover, from the tests performed in CERTH no deposition of any heavy material was observed in the storage vessels.

From the above discussions it can be concluded that in general the handling, storage and transport issues of the CPO seem to be not very different to those of the conventional heavy fuels. Of course it is preferable not to heat the CPO above 60 °C, in order to avoid secondary reactions that could change viscosity. It can be stored at room temperature, however, it is best to store it away from direct sunlight, in order to avoid reactions as mentioned above. Since the flash point is around 30 °C we need to take care and to handle it like a diesel fuel or preferable like gasoline.

B.4 CONCLUSIONS

In this deliverable we summarized the results from the work carried out in BioBoost towards optimization of biomass catalytic pyrolysis pathways in order to produce a valuable energy carrier (catalytic pyrolysis oil-CPO). Fifteen new catalytic materials were synthesized by Grace and tested in CPERI. From this pre-screening study the 3 best ZSM-5 catalysts plus 2 additional alumina type catalysts were selected and scaled up in GRACE in sufficient amounts for pilot scale testing. The new catalysts and five commercially available catalysts were tested in the pilot plant after a steam deactivation procedure. It was concluded that the best BioBoost catalyst performs better than the state of the art commercial catalyst producing about 1-2%wt more oil at the same oxygen yield. This result was fully validated using the other BioBoost feedstocks. Regarding feedstock optimization results it seems that the woody biomass is the best followed by the energy crop (Mischanthus) and the agricultural residue (wheat straw). As best feedstock and catalyst we are considering those that produce a higher yield of the bioenergy carrier at the same oxygen level. Regarding process optimization studies the C/B ratio seems to play a significant role since with excess catalyst the energy carrier overcracks and the yield is descreasing. We consider as optimum a C/B ratio of about 15 at the 500 °C pyrolysis temperature. It was also proved in this study that the catalyst deactivation plays an important role on the catalytic pyrolysis pathway. Both hydrothermal deactivation and ash metal poisoning have a strong detrimental effect on catalyst stability and performance. This is of major importance for follow up studies.

From the entire work performed in this deliverable sufficient amounts of bioenergy carrier were produced from the various catalysts and feedstocks and were fully characterized using routine and advanced characterization methods like 2DGC-TOFMS. The characterization showed that this bioenergy carrier (CPO) has significant advances regarding much lower oxygen, less TAN, more stability while it is a source of useful chemicals (like phenols and aromatics). All these properties are strongly related to the catalyst used in the catalytic pyrolysis process. For example for the production of the CPO with the highest phenolics concentration, catalysts FCC based ZSM-5, ZSM-5 w/matrix and high MSA appear to be the most efficient. On the other hand, the production of a CPoil with increased aromatics concentration is promoted by ZSM5-based catalysts such as ZSM-5 alternative matrix and FCC based ZSM-5.

Furthermore, one of the key characteristics of the CPO is that handling and storage of this EC do not differ significantly with that of the conventional fuels like gasoline, diesel or crude oil. The stability of the CPO is very satisfactory even after storage for more than 2 years. The acidity is very low compared to conventional bio-oils and not that strong even for carbon steels normally used in storage tanks. Its corrosiveness is classified as 1A at the copper corrosion tests and that means it has low corrosiveness. The CPO does not form deposits on the storage vessels for the entire period we stored them in CERTH (over 2 years).

Large amounts of this energy carrier were given to WP3 and WP5 for further downstream upgrading processes while full mass balances and technoeconomical data of this process were provided to WP6.

Abbreviations

C/B : Cat to Biomass Ratio

2DGC-TOFMS : Two-dimensional Gas Chromatograph – Mass Spectrograph TOF

TAN : Total Acid Number

ZSM-5 : Zeolite type catalyst

FCC : Fluid Catalytic Cracking

ZSA : Zeolite Surface Area

MSA : Matrix Surface Area

UCS : Unit Cell Size

CFB : Circulating Fluidized Bed

HCO : Heavy Cycle Oil

ICP-OES : Inductively Coupled Plasma Analyzer

Table B.1: Biomass Feed Characterization

Biomass Type	**Woody Biomass**	**Agricultural Residue**	**Energy Crop**
	Beechwood/ Lignocell	**Wheat Straw**	**Mischanthus**
C (dry wt%)	45.98	44.12	45.5
H (dry wt%)	6.39	6.16	6.00
O (dry wt% by dif.)	46.97	45.24	45.55
Ash (dry wt%)	0.66	4.48	2.5
Moisture (wt%)	7.63	8.71	5.30
Metals (ppm)			
K	452	4766	4650
Na	130	340	440
Mg	365	855	740
Fe	120	202	460
Al	-	305	-
Ca	1620	1955	1250

Table B.2: Properties of the catalytic materials scaled up by Grace

Catalyst ID	**#2464**	**#2465**	**#2467**	**#2468**	**#2469**
Catalyst Name	**ZSM-5 alternative matrix**	**Alumina matrix**	**ZSM-5 based FCC catalyst**	**ZSM-5 w/matrix**	**Alumina matrix CP3**
Deactivation	**Fresh**	**Fresh**	**Fresh**	**Fresh**	**Fresh**
TSA, m^2/g	112.18	68.21	86.74	110.06	90.89
ZSA, m^2/g	77.47	0	72.24	60.31	0
MSA, m^2/g	34.71	0	14.5	49.75	0
Z/M	2.23		4.98	1.21	
Deactivation	**Steaming (788°C/12h)**	**Steaming (788°C/12h)**	**Steaming (788°C/12h)**	**Steaming (788°C/12h)**	**Steaming (788°C/12h)**
TSA, m^2/g	88.65	36.41	103.6	114.13	70.93
ZSA, m^2/g	42.83	0	63.99	65.43	0
MSA, m^2/g	45.82	0	39.61	48.7	0
Z/M	0.93		1.62	1.34	

Table B.3: Contaminant metals impregnation and deactivation

Estimated time on stream (days)	**Fresh**	**2**	**10**	**20**	**30**	**40**	**50**
Metal	**%**						
MgO	0.10	0.16	0.33	0.55	0.73	1.0	1.3
P2O5	13.3	13.6	13.3	13.8	12.3	12.4	12.8
Na2O	0.19	0.23	0.34	0.52	0.61	0.76	0.92
CaO	0.08	0.25	0.89	1.7	2.2	2.6	3.3
K2O	0.14	0.45	1.6	3.2	3.9	5.0	6.7
	m^2/g after steaming at 815°C for 24 hrs						
Total Surface Area	101	97	67	29	8	6	5
Zeolite Surface Area	62	66	49	25	4	3	2
Matrix Surface area	39	31	18	4	4	3	3

Table B.4: Effect of catalyst deactivation on product yields

Products	Steam deactivated ZSM-5 based FCC catalyst	Steam deactivated ZSM-5 based FCC catalyst with metals at the end of the long run test
Biooil, %wt	25	27.9
Coke, %wt	19.5	18.1
CO, %wt	18.5	17.3
CO_2, %wt	10.75	11.1
H_2O (%wt)	25	24.9
O_2 in oil, %wt	17	19.6
Deoxygenation, %wt	91	88.5

Table B.5: Bioboost biooils analyses produced by different new (BIOBOOST) catalysts and Lignocel feed

Catalyst	Commercial ZSM-5	ZSM-5 based FCC catalyst	ZSM-5 catalyst w/ matrix	ZSM-5 catalyst alte/matrix	Alumina matrix	Alumina matrix CP3
Water, %wt of bio-oil	6.51	4.70	5.48	7.49	5.46	1.44
C, %wt of dry bio-oil	74.30	77.74	78.29	72.44	75.35	85.44
H, %wt of dry bio-oil	7.38	6.38	6.13	5.19	5.86	6.61
O (by dif.), %wt of dry bio-oil	18.33	15.88	15.58	22.38	18.79	7.95
Density,g/ml	1.09	1.09	1.10	1.10		
Calorific value (HHV, MJ/kg)	29.50	31.83	31.79	30.8	29.69	35.08
TAN, mgKOH/g	38.09	25.00	29.24	47.89	41.59	0.95
MCRT, %wt	17.79	14.15	12.82	20.84		

Table B.6: Bioboost biooils analyses produced by Lignocel feed and Wheat straw

Catalyst	**Commercial ZSM-5**		**ZSM-5 based FCC catalyst**	
Feed	**Lignocel**	**Wheat straw**	**Lignocel**	**Wheat straw**
C, %wt	74.30	74.15	77.74	77.50
H, %wt	7.38	6.21	6.38	6.26
O, %wt (by difference)	18.33	19.64	15.88	16.24
H_2O (%wt)	6.51	6.66	4.70	5.53
Density (g/ml)	1.09	1.10	1.09	1.10
HHV (MJ/kg)	29.50	29.30	31.83	31.17
TAN (mgKOH/g)	38.09	43.44	25.00	24.24
MCRT (%wt)	17.79	18.51	14.15	12.83

Table B.7: GCxGC-ToFMS quantification of CPoils

Catalyst: ZSM-5 **Biomass: lignocel** **Organic Phase**		**Catalyst FCC based ZSM5** **Biomass: lignocel** **Organic phase**		**Catalyst FCC based ZSM-5** **Biomass: wheat straw** **Organic Phase**	
Compound	*% w/w*	*Compound*	*% w/w*	*Compound*	*% w/w*
p-Xylene	2.99	p-Xylene	4.77	Benzene, 1,3-dimethyl-	4.50
1,2-Benzenediol	2.18	Phenol	2.47	Phenol	2.85
2-Cyclopenten-1-one	2.06	Toluene	2.11	Toluene	2.57
Phenol	1.84	Naphthalene, 2-methyl-	2.09	Phenol, 3-methyl-	2.20
Phenol, 3-methyl-	1.64	Vanillin	2.08	2-Cyclopenten-1-one	1.64
Phenol, 2,5-dimethyl-	1.12	Phenol, 3-methyl-	1.93	Vanillin	1.47
Toluene	1.10	Phenol, 2,5-dimethyl-	1.80	Phenol, 2-methyl-	1.22
Benzene, 1,2,3-trimethyl-	1.03	Phenol, 2-methyl-	1.56	Benzaldehyde	1.20
Benzofuran, 2-methyl-	1.03	2-Cyclopenten-1-one	1.55	Ethylbenzene	1.11
Phenol, 2-methyl-	1.00	Benzene, 1,2,3-trimethyl-	1.30	Phenol, 2,5-dimethyl-	1.08
Total $_{\text{Top 10 compounds}}$ (% w/w)	15.98	Total $_{\text{Top 10 compounds}}$ (% w/w)	21.64	Total $_{\text{Top 10 compounds}}$ (% w/w)	19.84
Total (% w/w)	48.37	Total (% w/w)	54.26	Total (% w/w)	42.34

Table B.8: Sum of %wt of quantified compounds per group

CATALYST	**AR**	**ALI**	**PH**	**FUR**	**ETH**	**ALD**	**KET**	**PAH**
high ZSA	1.52	0.55	13.74	2.46	0.31	4.45	7.64	1.50
high activity	2.87	0.75	15.02	2.89	0.41	4.23	9.17	3.16
silica sol	0.98	0.29	10.37	1.39	0.30	4.33	5.55	0.65
high MSA	3.14	0.76	17.30	3.20	0.41	4.75	9.59	2.99
ZSM-5	12.69	2.38	14.56	3.18	0.16	3.97	8.62	2.27
Alternative matrix ZSM-5	17.66	0.13	14.58	1.44	0.02	1.63	2.53	4.10
FCC based ZSM-5	16.35	0.20	20.55	2.07	0.08	5.39	5.18	4.34
ZSM-5 w matrix	12.15	0.42	18.18	2.13	0.03	3.04	4.12	2.63
FCC based ZSM-5 (wheat straw)	15.46	0.81	14.26	1.78	0.02	2.09	5.91	1.85

Table B.9: Storability of CPoil

	0 months	6 months	12 months	18 months	22 months	27 months	Accelerated ageing at 40^{o}C for 7days	Accelerated ageing at 80^{o}C for 24h
C, %wt	69.66	68.68	68.07	69.27	67.88	68.85	68.19	68.66
H, %wt	7.8	7.17	7.27	5.7	6.12	7.53	7.00	7.04
O, %wt (by difference)	22.54	24.13	24.65	25.01	25.98	23.61	24.79	24.28
S (ppmwt)	n.a.	157	145.3	154.2	157.2	146.8	155.5	150.3
Density (g/mL)	1.1206	1.1237	1.128	1.1317	1.1297	1.1308	1.1283	1.1269
Viscosity, 50^{o}C (cSt)	13.6913	16.2569	20.5251	25.8866	25.787	28.1242	23.9342	20.3159
HHV (MJ/kg)	29.5161	29.2492	29.6627	29.3934	29.3636	29.1754	29.521	29.2832
TAN (mgKOH/g)	40.4036	41.5490	39.1287	40.9398	40.5965	41.0389	44.1220	41.4673
H_2O (%wt)	6.5	6.4	6.1	5.8	7.8	7.5	6.9	7.1
Copper strip Corrosion	n.a.	1A	1A	1A	1A	1A	1A	1A

Table B.10: Analysis of initial and aged biooils produced with BioBoost catalysts

	Initial samples			**Aged at 40^{o}C for 7days**		
	Lignocel with the commercial ZSM-5	Lignocel with ZSM-5 w/matrix	Wheat straw with FCC based ZSM-5	Lignocel with the commercial ZSM-5	Lignocel with ZSM-5 w/matrix	Wheat straw with FCC based ZSM-5
C, %wt	69.83	72.25	71.01	72.61	72.88	73.41
H, %wt	7.81	8.36	7.88	7.89	7.72	7.78
O, %wt (by difference)	22.34	19.37	21.09	19.47	19.38	18.79
S (ppmwt)	213	165.3	160.2	287.2	173.3	169.5
Density (g/mL)	1.1149	1.0973	1.0999	1.1174	1.0961	1.1008
Viscosity, 50oC (cSt)	24.5645	10.1812	11.9506	24.6838	11.0128	13.3185
HHV (MJ/kg)	30.3539	31.8607	31.1734	31.1536	31.5186	31.2837
TAN (mgKOH/g)	34.401	28.1659	27.4865	30.5251	29.0597	29.2399
H_2O (%wt)	5.1554	5.1388	5.5142	5.3314	4.7168	4.8803
Flash point (^{o}C)	29.5	30.5	22.5	33.5	29.5	23.4
Copper strip Corrosion	1A	1A	1A	1A	1A	1A

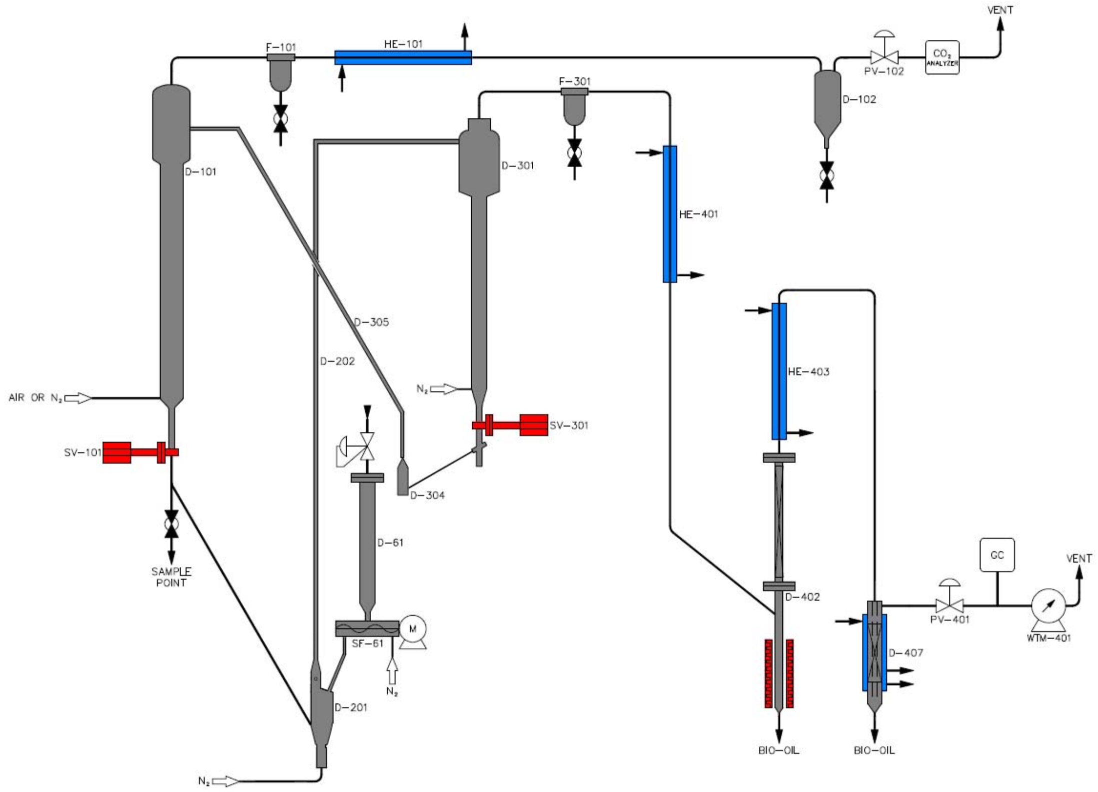

Figure B.1: Biomass Catalytic Pyrolysis Pilot Plant Unit

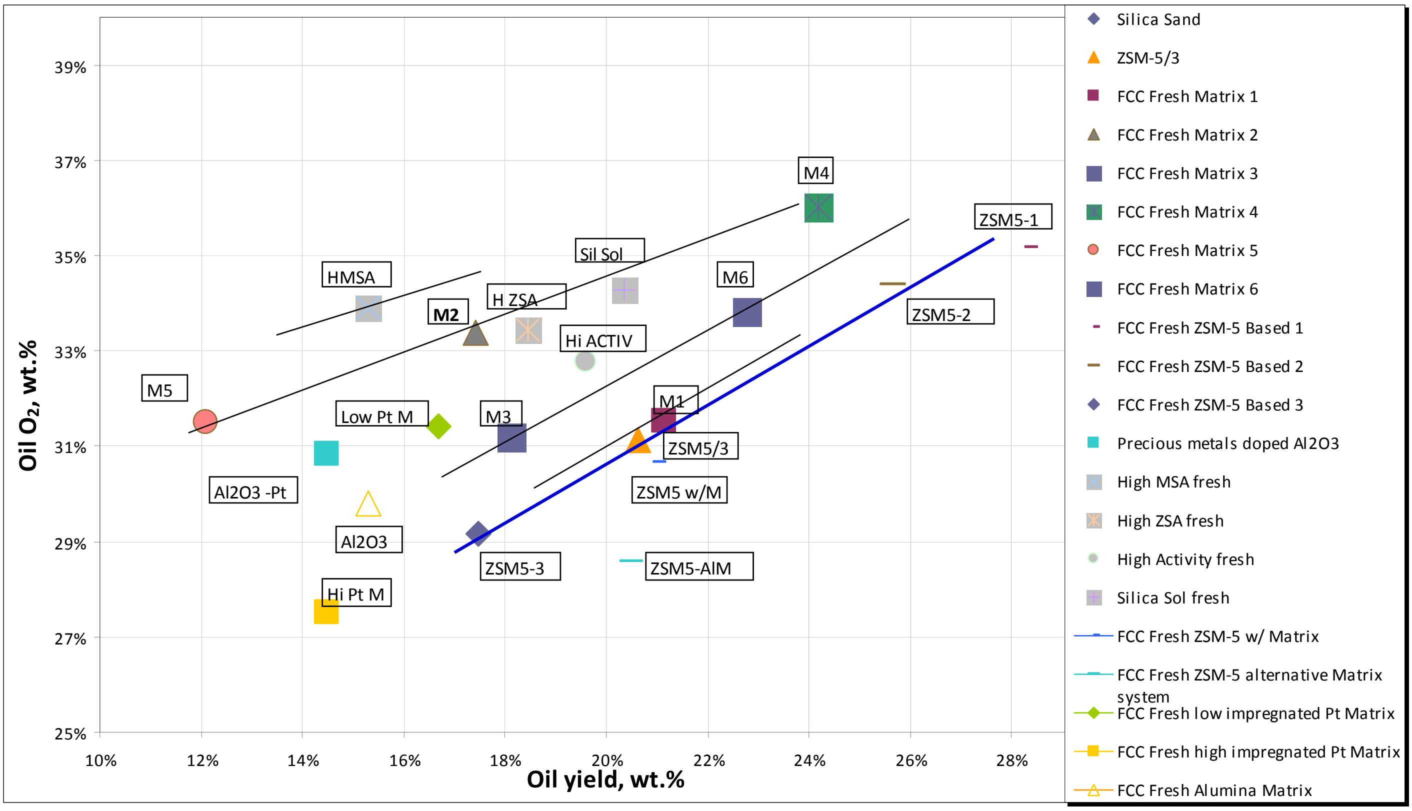

Figure B.2: Oxygen in Organic Oil vs Organic Oil yield (catalyst pre-screening studies, dry basis)

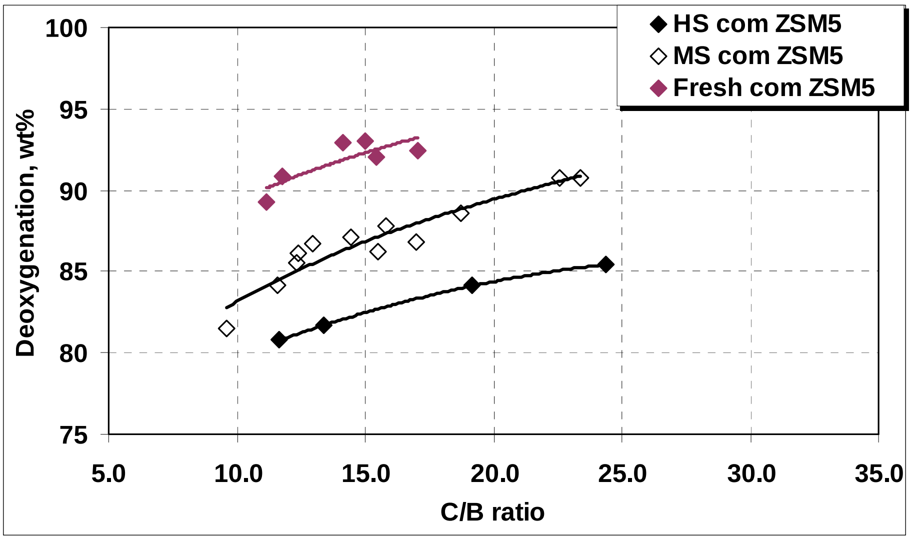

Figure B.3: Deoxygenation vs C/B ratio (selection of deactivation protocol)

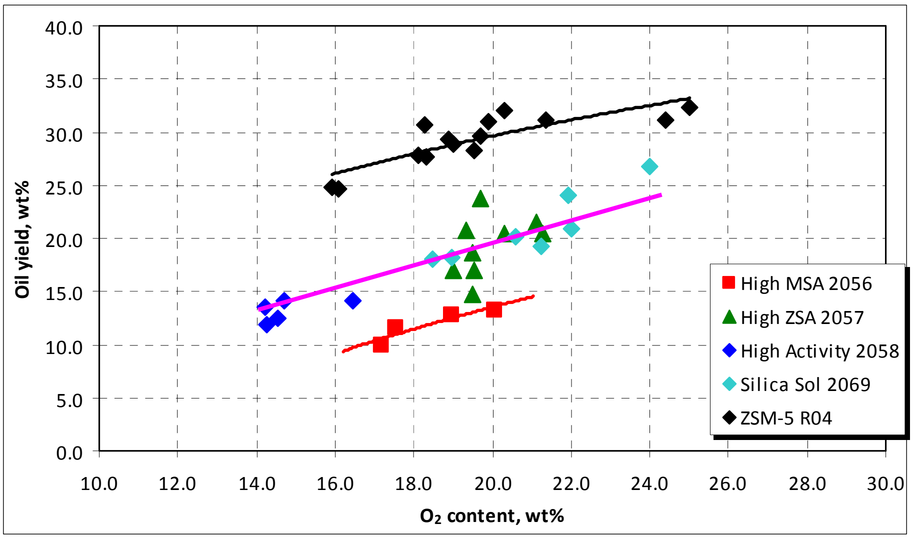

Figure B.4: Organic Oil yield vs Oxygen content (pilot scale catalysts evaluation studies, dry basis)

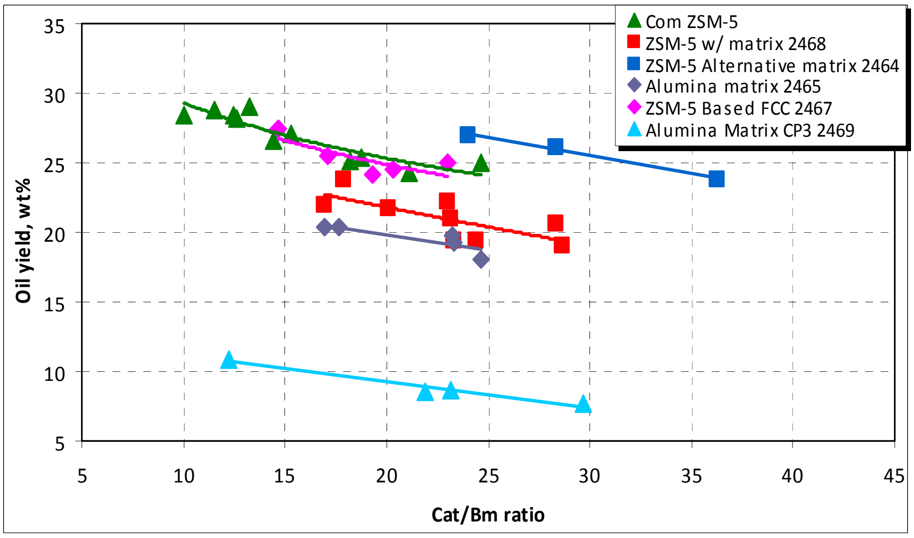

Figure B.5: Organic Oil yield vs C/B ratio (pilot scale catalysts evaluation studies, dry basis)

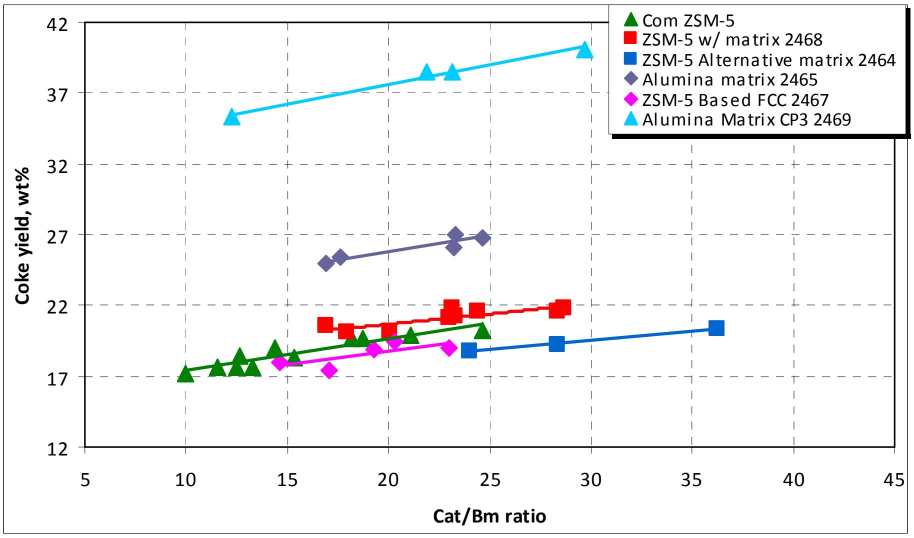

Figure B.6: Coke yield vs C/B ratio (pilot scale catalysts evaluation studies)

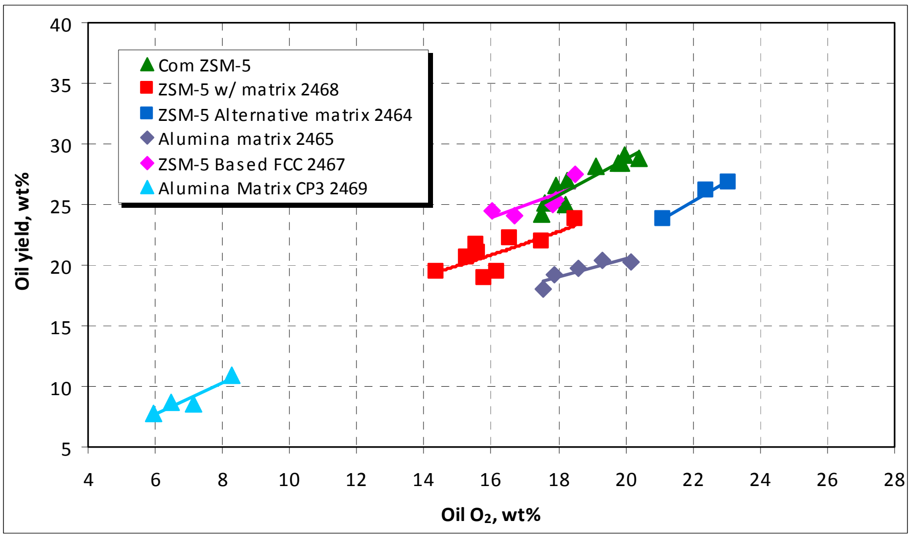

Figure B.7: Organic Oil yield vs Oxygen content (pilot scale catalysts evaluation studies, dry basis)

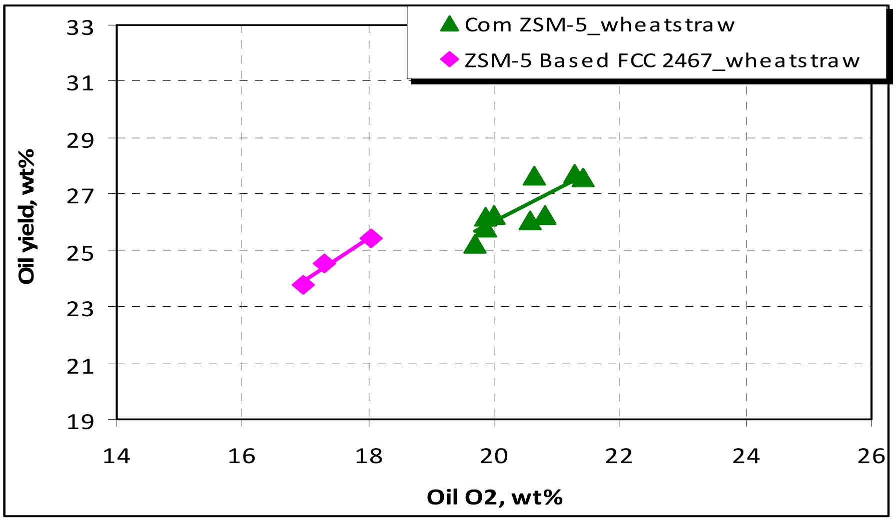

Figure B.8: Organic Oil yield vs Oxygen content (pilot scale catalysts evaluation studies, dry basis)

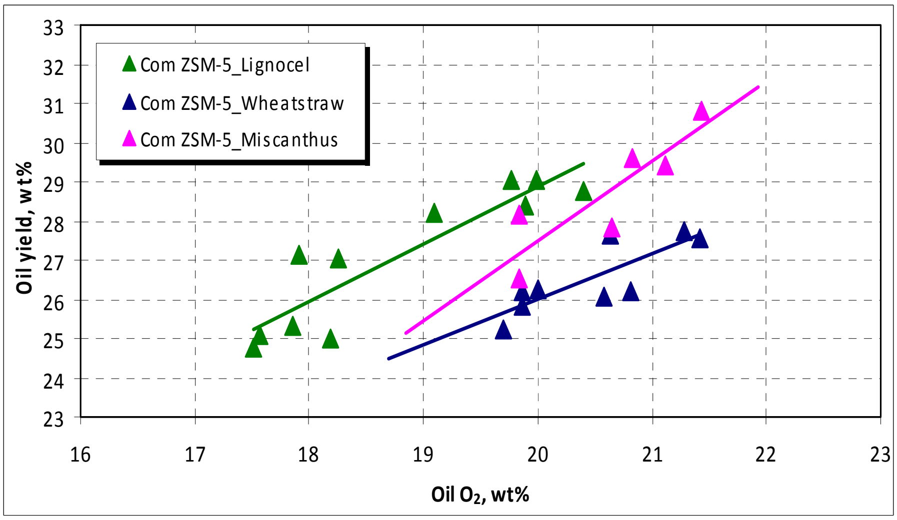

Figure B.9: Organic Oil yield vs Oxygen content (pilot scale catalysts evaluation studies, dry basis)

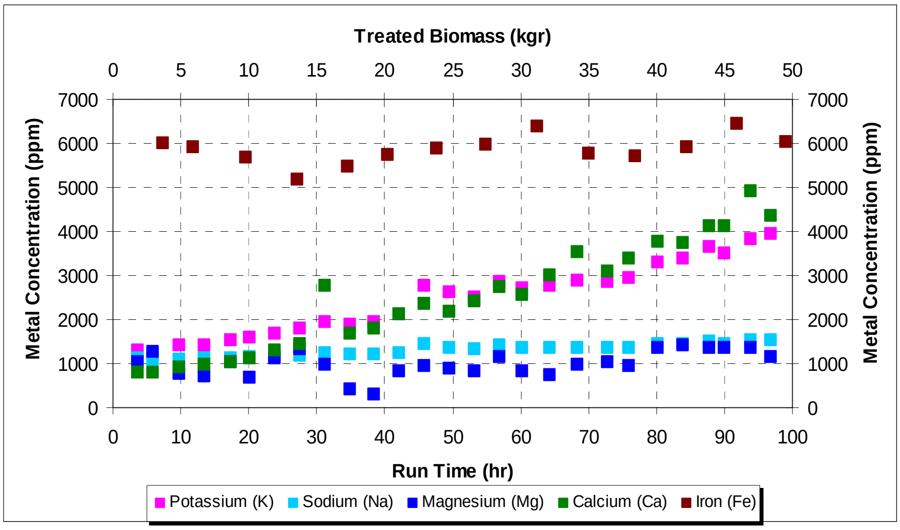

Figure B.10: Measured Concentrations of Metals (K, Na, Mg, Ca, Fe) on the catalyst with biomass run time or treated biomass

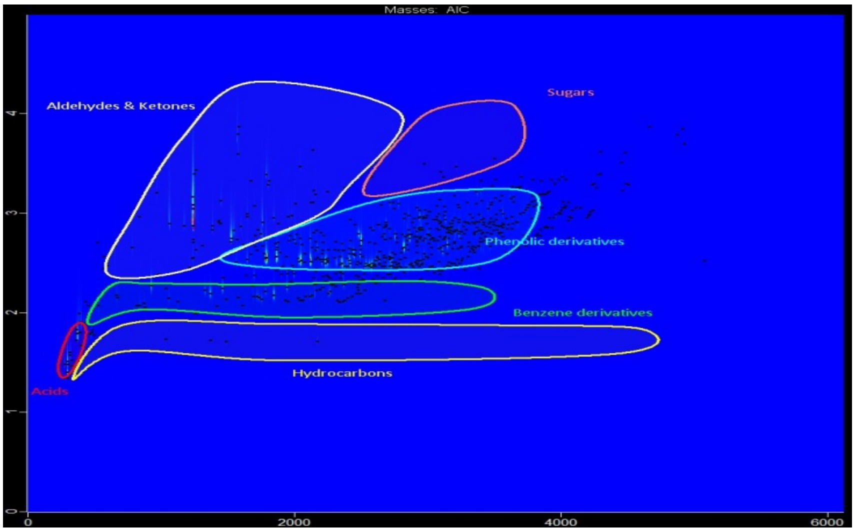

Figure B.11: GCxGC-ToFMS chromatogram of CPoil from com. ZSM-5 catalyst

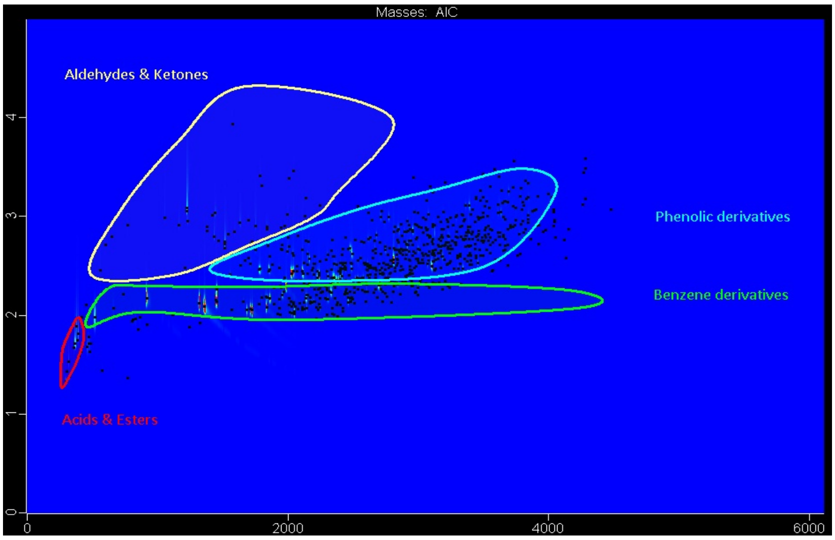

Figure B.12: GCxGC-ToFMS chromatogram of CPoil from catalyst FCC based ZSM-5

APPENDIX C

HYDROTHERMAL CARBONIZATION

(AVA-CO2)

Report

C.1 INTRODUCTION

In this deliverable the tasks done as described in T2.3 of DOW_BioBoost_(282873)_2011-10-14 are summarized for HTC:

- the wet HTC-coal produced in T2.2.3 is dried in the most economic level for storage, transport and application
- AVA-CO2 Forschung provides 3 concepts for medium and long term storage and logistics taking into account particle size, humidity and safety regulations.
- Following the process scheme of AVA-CO2, there is an additional step required between the reaction (see batch reactors unit 300) and the drying of the wet HTC-coal. HTC-coal leaves the HTC reactor in a wet phase (slurry). In order to dry it, it is separated by several filtration technologies from the slurry (unit 500). The result is a wet HTC-coal and a process water still containing some HTC-coal and pollutants. This water has to be treated further in order to dispose it with the wastewater system (unit 800).

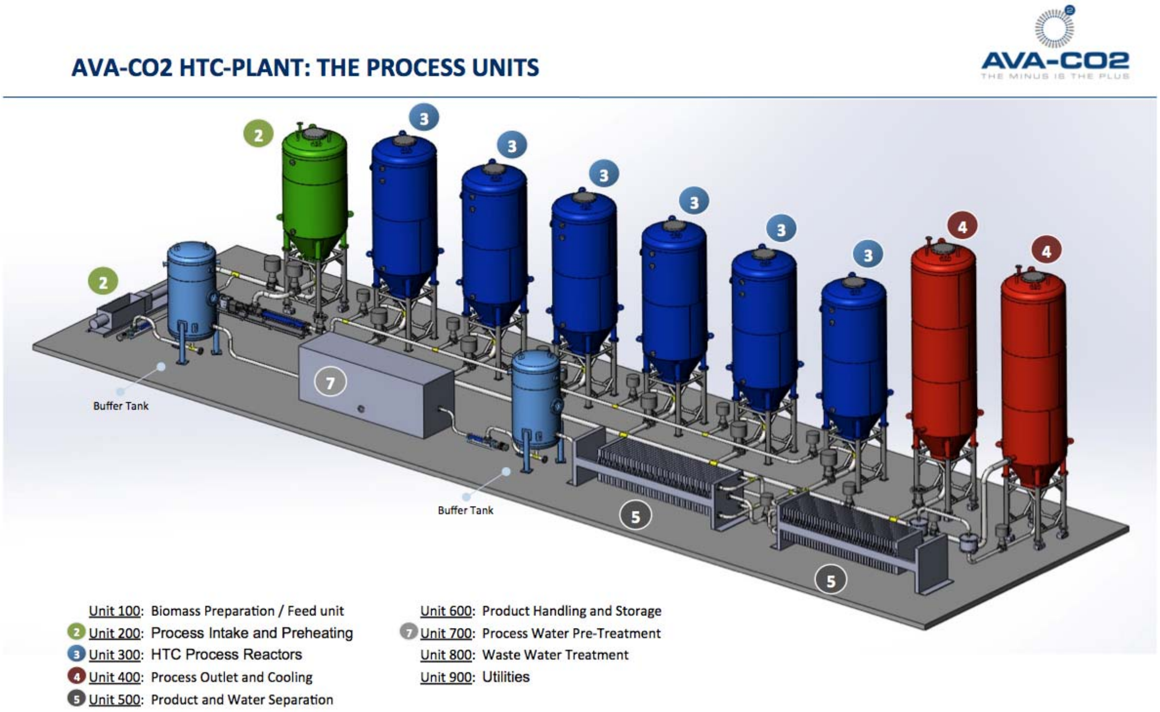

Figure C.1: Process Units of AVA-CO2 HTC plant

This part of the HTC process will be handled as a prerequisite of the drying technologies described.

C.2 FILTRATION TECHNOLOGIES TESTED AND APPLIED

C.2.1 Definition of Target

Dewatering the HTC slurry results in a wet biocoal which is treated further by drying and giving it is final shape as either dust, pellets or cakes and on the other side, there is a process water which hast o be treated further for disposal or reuse in the HTC plant.

Figure C.2: Process water from the chamber filter press

The tests done at AVA-CO2 Forschung aimed at a technically and economically feasible technology which is valid for the biomasses used and where the water is cleaned up to a level which allows disposal to public sewage water system.

Two systems have been tested:

- A nano filtration plant (NF) and
- a membrane bio reactor (MBR) for biological post-processing

The MBR's task is to prove the biological decomposability of the HTC permeate and to capture eventual load peaks of the NF plant.

The decision for these two technologies is based on prior studies and analyses of AVA CO2 for process water treatment.

C.2.2 Nanofiltration

The remaining process water contains a high amount of precious dissolved organic carbon (DOC). In contrast to chemical and biological cleaning, physical separation technologies leave the DOC unchanged.

The technical solution applied is a concentration of the not yet condensed HTC biocoal particles with a membrane technology. This results in a permeate, which contains only a small volume of DOC, which is easily reduced in a biological way.

The DOC particles in front of the membrane are concentrated and can be recycled. Recycling reduces the fresh water volume for the next HTC process and adds HTC particles. These particles polymerise during the next HTC reaction and build "crystallization seeds" for the condensation reaction.

C.2.3 Membrane Bioreactor (Optional Permeate-Processing)

Membrane processing is a combination of classical aerobic cleaning and membrane filtration to separate slurry from clean waste water. This technology replaces space demanding cleaning pools by small reactors. The usage of MBRs extend the hydraulic retention period, thus allowing a high degradation rate of the DOC.

C.3 TESTS AND ANALYSIS

The first pilot test could prove the performance and process stability of nanofiltration. Against our expectation, there was a high amount of slowly degrading DOC matter in the permeate. Tests carried out with different dilution rates suggest a constant elimination rate of the organic load.

The quality of the permeate depends on the process water load and the membrane used in the nanofiltration plant. Therefore the test was repeated with a different membrane. With a high level of retention for middle sized molecules, the more difficult degrading DOC matter should be better retained by this membrane. Also the batch recipe was adjusted to reduce the loading of the process water.

C.3.1 Tests

Four batches have been carried out under identical reaction parameters. The resulting process water therefore differs only in the selection of sewage sludges[1] and added process water. All batch slurries have been dewatered by the membrane filter press (see chapter on "Drying") separately in order to prevent a mixture of the batch slurries. The resulting slurries were prepared in the basis plant of the nanofiltration and the permeate stored in IBCs. Then the permeate was introduced to the membrane bio reactor to be treated aerobe without nitrification / de-nitrification. The chart shows a simplified flow chart with data of the major streams.

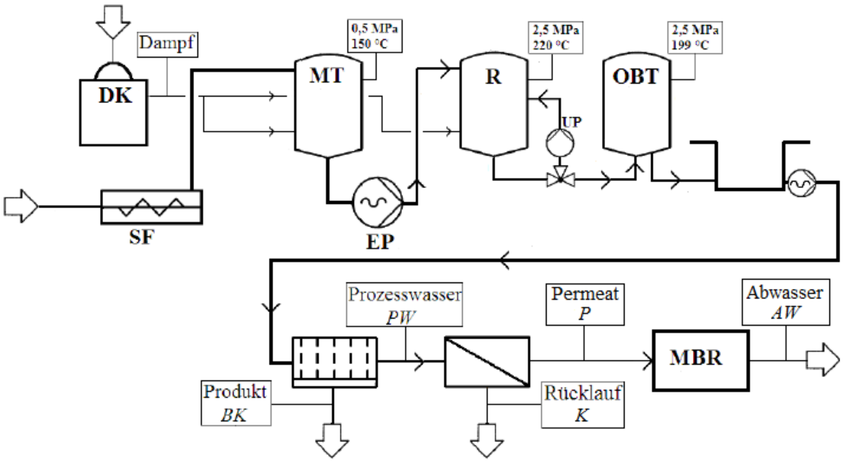

Figure C.3: Flow chart of the filtration tests

C.3.2 Data collection and Analytics

There was no PC-supported data storage possible at the plant. Therefore the sensors have been protocolled manually. Data analysed: pH, conductivity, CSB, DOC, TNb, NH4-N, NO3-N, NO2-N, PGes, PO4-P.

C.3.2.1 Analysis of parameters of mass throughput

Based on the process steps as shown above in the flow chart, the fields of activities have been defined:

- Daily drawing of samples was done by AVA-CO2 Forschung
- Analysis of the biomass, biocoal, and process water of the HTC batches have been done by an external lab
- DOC degradation tests of the HTC permeate was done by AVA CO2

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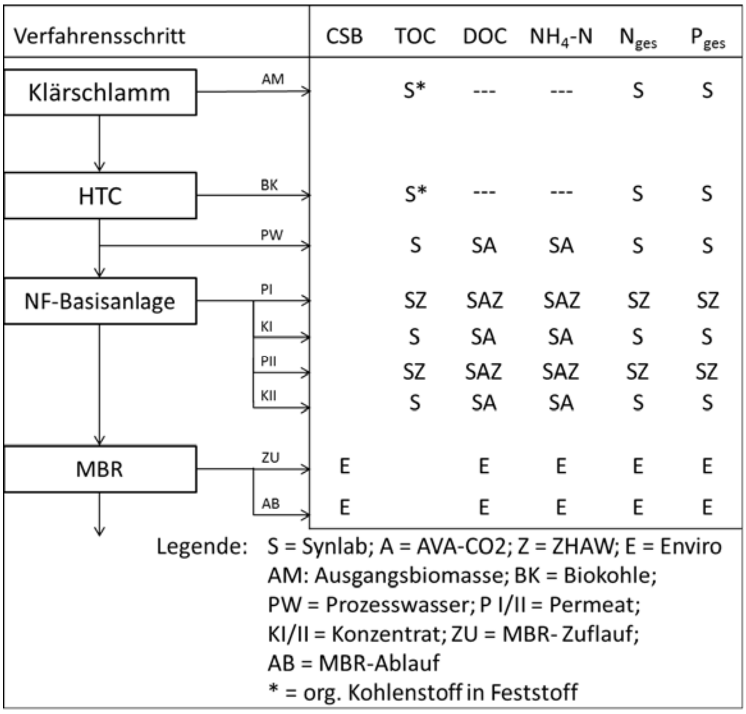
[1] Sewage sludge is regarded being the most critical material for HTC. A filtration plant that works for sewage sludge permeate will work for less critical permeate stemming from brewery spent grains and / or organic household waste as well.

Analysis of throughput and performance was done by another external lab

The following chart summarizes the results.



Verfahrensschritt		CSB	TOC	DOC	NH_4-N	N_{ges}	P_{ges}
Klärschlamm	AM		S*	---	---	S	S
HTC	BK		S*	---	---	S	S
	PW		S	SA	SA	S	S
NF-Basisanlage	PI		SZ	SAZ	SAZ	SZ	SZ
	KI		S	SA	SA	S	S
	PII		SZ	SAZ	SAZ	SZ	SZ
	KII		S	SA	SA	S	S
MBR	ZU	E		E	E	E	E
	AB	E		E	E	E	E

Legende: S = Synlab; A = AVA-CO2; Z = ZHAW; E = Enviro
AM: Ausgangsbiomasse; BK = Biokohle;
PW = Prozesswasser; P I/II = Permeat;
KI/II = Konzentrat; ZU = MBR- Zuflauf;
AB = MBR-Ablauf
* = org. Kohlenstoff in Feststoff

Figure C.4: Analyses carried out and responsibilites

C.4 NANOFILTRATION (BASIC PLANT FOR PROCESS WATER TREATMENT)

C.4.1 Pilot Plant used

For the tests, a modified filtration plant from OSMO Membrane Systems was used. The membranes used were made out of a polyamid-composite with a membrane filter surface of 7.5 m^2.

Starting from a collecting container (i.e. feeding tank) a feeding pump PU002 pumps the process water feed through pre-filter F001. If needed for better filtration results, a heat exchanger cools a part of the feed after F001.

The high pressure pumps PU003 and PU004 increase pressure on the feed side to overcome the osmotic pressure of the liquid. Then the membranes separate the feed into permeate and concentrate.

In order to prevent mechanical and/or thermal overload, sensors measure the data of some critical components:

- Pre-pressure filter: an increasing thickness of the coal cake during the filtration produces a sinking pressure. If a predefined pressure difference is reached, the plant shuts down
- Membrane: for a safe operation of the membrane, pressure and temperature have to be supervised. Especially on the concentrate side a pressure loss is critical and can damage the membrane
- Permeate / Concentrate: important separation properties of the membrane can be calculated on the basis of measured electrical conductivity

The following chart shows an R&I design and a photo of the pilot plant and the major components mentioned.

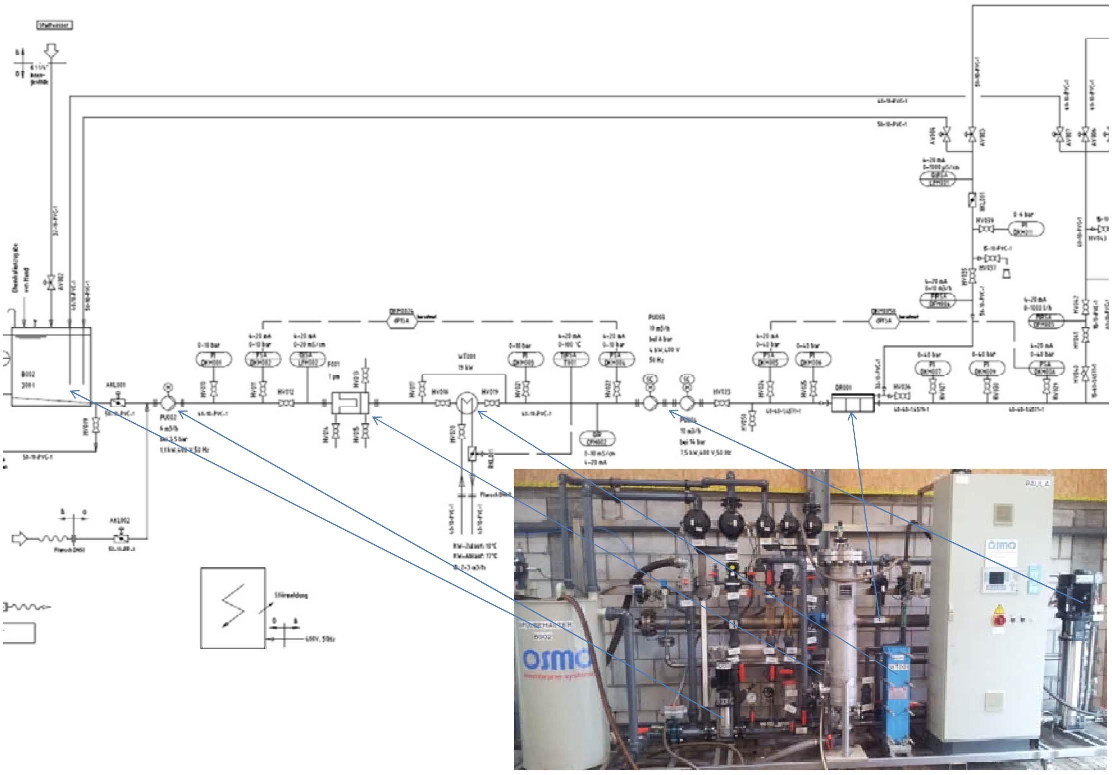


Figure C.5: NF basic plant as R&I scheme and photo

C.4.2 Results of Process Water Processing

C.4.2.1 Operation, Runtime and Dysfunctions

During tests no unplanned safety shut downs occurred. Short interruptions were necessary for the exchange of pre filter cartridges and cleaning cycles for the membrane. Operation without preparation and pilot testing took 21 days.

In analogy to the first pilot tests a concentrate refeed was necessary to increase concentration. Because solubility of the biocoal in the retentate stopped, it dropped out. Without a post filter, the pre filter would have been the only solid-liquid filtration in the system. The increasing pressure difference resulted in a safety shutdown.

A large scale layout of this technicum plant does not require a refeed of concentrate, thus the formation of coal in the pre filter system can be excluded, which is important for an automatic uninterrupted operation. Due to the cascading construction architecture of the membrane modules cleaning cycles can be run per module without requiring a shutdown of the whole plant.

C.4.2.2 Performance of the Membrane

The whole testing period was characterised by a high level of process stability with respect to the membrane performance. With the exception of PII(2), the nano filtration (NF) basic plant worked with all kinds of process waters, esp. biocoal from brewery spent grains and organic municipal waste, but also other kinds of biocoal. An exception was permeate PII(2), which passed the NF basic plant in 2 cycles. It was an extremely toxic sewage sludge from the chemical and automotive industry.

Flusswerte (Flux)

Membrane flow performance (Flux = F_P) is being calculated from produced permeate volume $\dot{V}$, per m^2 and per hour.

$$F_P = \frac{\dot{V}}{A \cdot t} \quad \left(\frac{1}{m^2 \cdot h}\right)$$

A = membrane filter surface [m^2], t = time [h]

- **Phase I (P1):** Pre filter cartridges had to be changed and cleaned twice. This required 57 min, which is negligible taking into account the whole run time. Flow performance remains constant, even after resuming the operation. Taking into account the fouling potential, a flux of 5 l/(m^2·h) is possible.
- **Phase II (P2):** After the first run through, the permeate (P1) showed a DOC similar to untreated process water. During the 2nd run a high yield of the concentrated permeate could be reached without any problems. The average flux of the 1st step was < 1.5 l/(m^2·h), the 2nd step 9.5 l/(m^2·h). An analysis of the flux values over a period of 10 days allows the conclusion, that a stable operation with a flux of 7.5 l/(m^2·h) is possible for up to 30 days without cleaning.
- **Phase III (P3):** The medium flux was a little lower than P1 with 6.7 l/(m^2·h). Taking into account an operation period of 450 h the risk of conditioning therefore is limited. At the end of the concentration process, the flux stabilized at 5 l/(m^2·h).
- **Phase IV (P4):** The middle flux was identified at 7 l/(m^2·h). It has to be noted, that between P3 and P4 the NF plant was only rinsed, the membrane was not cleaned. The analysis suggests a flux of 2.5 l/(m^2·h) after an operation period of 30 days (based on P3 and P4).

Generally speaking, the performance of the membrane was unexpectedly high. The major reasons for this are the general low load of the process water (what DSM judged as economically not interesting for the extraction of by-products) and a low load of particles in the process water. Furthermore, the feeding tank was filled with low flow rates, to avoid a stirring up of the already separated coal particles. The table shows the major results.

Table C.1: Produced permeate of 4 batches

Designation	Permeate [m^3]	Yield [%]	Flux [l/(m^2*h)]
Permeate 1 (PI)	4.40	67.67	7.0
Permeate 2 (PI)	3.81	49.51	1.5
Permeate 2 (PII)	3.09	77.26	9.5
Permeate 3 (PI)	3.30	66.03	6.7
Permeate 4 (PI)	3.24	65.38	7.0

Permeability

Permeability L_P is defined as the standardization of the flux with the help of the trans membrane pressure. It represents the pressure difference between feed and concentrate to permeate. The higher pressure is calculated from the medium of the pressure before (feed) and after (concentrate) the membrane modules. Because the permeate flows out freely, the pressure is equivalent to the atmospheric pressure.

$$L_P \quad \frac{F_P}{\Delta p} \quad \frac{\frac{\dot{V}}{A \cdot t}}{(p_{Eingang} \quad p_{Ausgang}) \quad p_{Permeat}} \left| \frac{l}{bar \cdot m^2 \cdot h} \right|$$

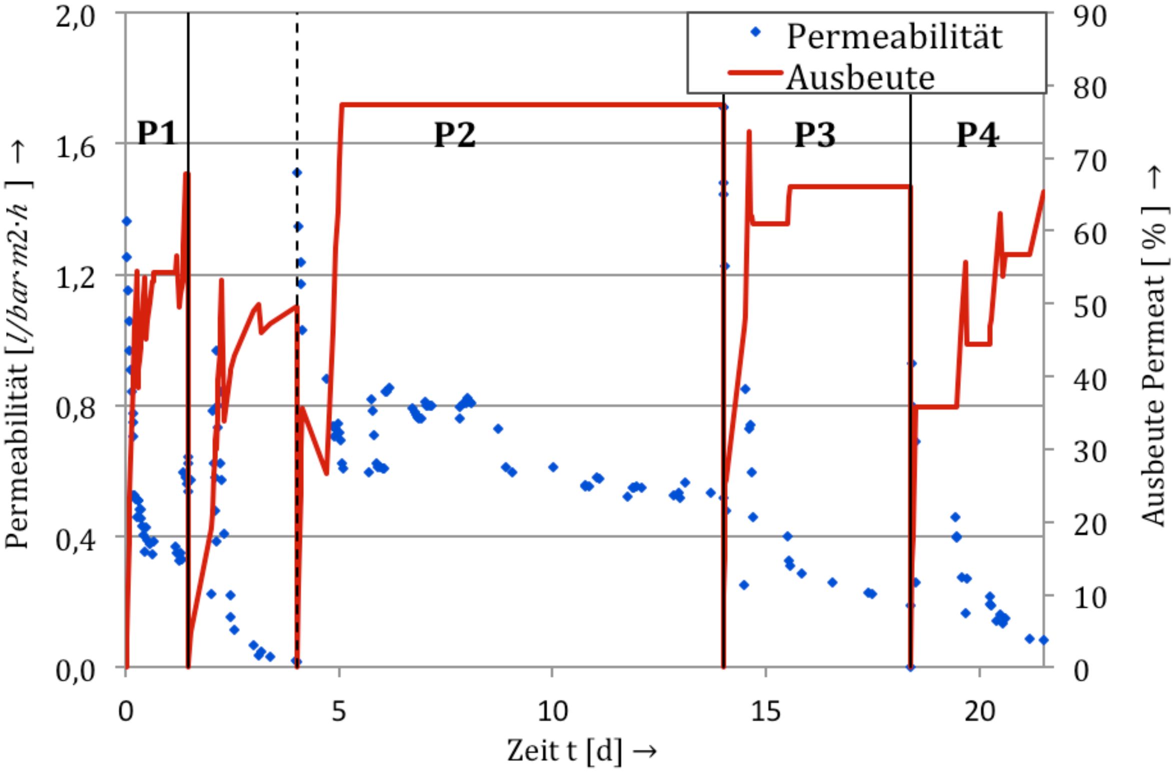


Figure C.6: Permeability and permeate yield of the phases in time

The concentrate was circulated and filled up with fresh process water. Adding process water results in a concentrate, because the overall volume is increased. “Yield permeate” therefore shows variations in the beginning of each phase.

Reactivation of membrane (water value)

The long term contact of the membrane with the organic solution leads to a layer formation on the membrane surface after some time. In contrast to the anorganic or biological fouling, this layer is made out of biocoal particles. Due to the hydrophilic properties of the biocoal, it can be cleaned without any rests by a conventional membrane cleaning.

The performance of the membrane was analysed by the water value before and after cleaning.

The decrease of the flow value of the membrane is within 3.75%. Water value of the 2nd cleaning was 82.5%, significantly lower than after the 1st cleaning. Reason was the short contact time of the cleaning solvent with the membrane surface. The cleaning period of 10 instead of 30 minutes was too short for a complete cleaning of the membrane. From the table below can be seen, that the membrane could be recovered almost completely after 628 hours of continuous operation.

Table C.2: Water values of the membrane after cleaning, depending on the contact time with process water

Designation	Value [l/h]	Operation hours [h]	Membrane Performance [%]
Water value new	1700.0	0	---
Water value 1st cleaning	960.0	126	100.00
Water value 2nd cleaning	792.0	455	82.50
Water value 3rd cleaning Reinigung*	924.0	629	96.25

** after ending the test, the plant was still used for 3 days*

C.4.2.3 Quality of the produced permeate

The daily permeate samples were taken directly from the permeate stream and not form the mixed permeated. Thus, the DOC analysis was could be made under operation conditions.

For a better interpretation of the development of the DOC load in dependency of the concentration factor the molar permeability $L_{P,mol}$ is used.

$$L_{P,mol} = \frac{L_P \cdot \rho}{M(C)} = \frac{L_P \cdot 1000\,\frac{g}{l}}{12\,\frac{g}{mol}} \left(\frac{mol}{bar\ m^2\ h} \right)$$

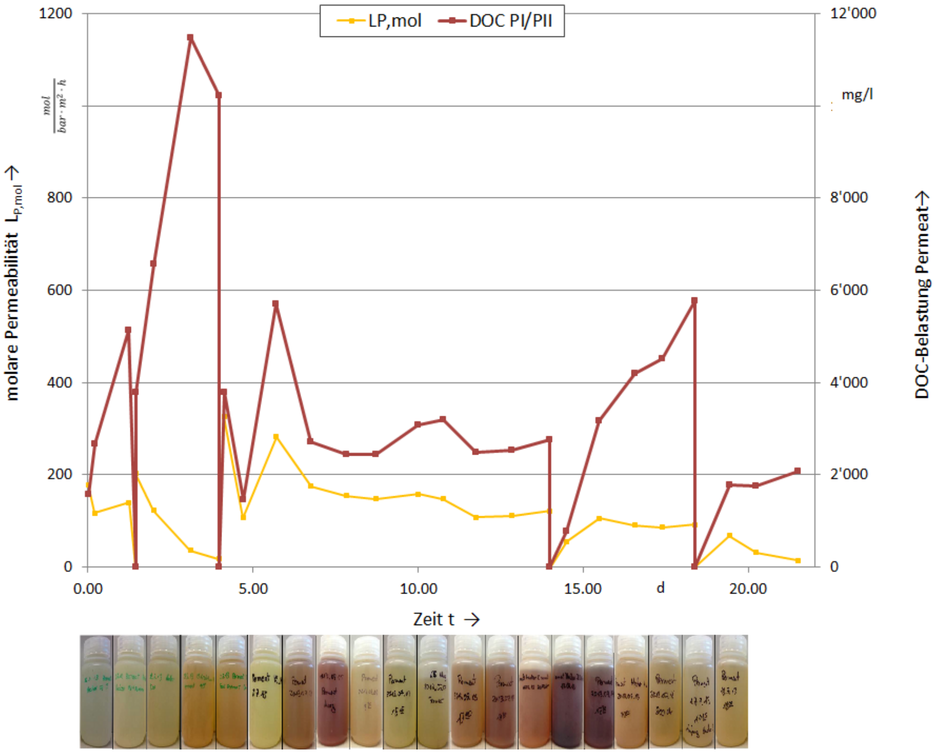


Figure C.7: DOC-load in permeate and molar permeability along testing time with photos of the permeate taken per day

Interpretation

Permeate with a high $L_{P,mol}$ and a low DOC has a low load. This is indicated by color, odour, smell and electrical conductivity.

Table C.3: DOC measured and NH4-N load in HTC-Permeate with a low load of the plant

Designation	Time [h]	DOC [mg/l]	NH_4-N [mg/l]
Permeate 1 (PI)	0.35	1575	403.1
Permeate 2 (PI)	13.00	3790	1073.4
Permeate 2 (PII)	3.75	1460	1007.9
Permeate 3 (PI)	12.25	788	634.5
Permeate 4 (PI)	25.00	2‘330	911.9

- The concentration of salt and other matter increases with a sinking concentration volume exponentially. If membrane still stand is short, no fouling of the membrane surface can be observed. In this case the development of $L_{P,mol}$ is an indication of a fast increasing osmotic pressure.
  This can be observed during all phases and especially during the first concentration of P2. The concentrate showed with 64000 mg/l a DOC load which was 2.5 times higher than normal. Taking into account the high load, it seems to be plausible that yield was only 50%.
- During stationary operation a constant DOC load with sinking $L_{P,mol}$ represents the fouling potential of the process water.

DOC Concentrations of Permeate

Waste water quality of the permeate is defined by the level of the DOC value of the permeate mixture produced. All permeates produced had a lower level than required for disposal. The exception was permeate II, where a second concentration was tried with the same membrane. This is not possible as results show. Therefore the DOC concentration after the second concentration process is still above 4300 mg/l.

Table C.4: Results of DOC measurements in HTC permeate

Sample	Operating time [h]	Phase	Permeate yield [%]	DOC [mg/l]
Permeate PI aus Batch 2013.05.21.1-HTC-0.1	125.68	P1	67.67	2550 2200
Permeate PI aus Batch 2013.06.20.1-HTC-0.1	209.67	P2	49.51	5250
Permeate PII aus Batch 2013.06.20.1-HTC-0.1	448.90	P2	77.26	4300 3350
Permeate PI aus Batch 2013.06.27.1-HTC-0.1	554.20	P3	66.03	2300
Permeate PI aus Batch 2013.07.04.1-HTC-0.1	628.95	P4	65.38	2100

C.5 MEMBRANE BIOREACTOR (OPTIONAL PERMEATE-TREATMENT)

C.5.1 Pilot Plant used

The membrane bio reactor (MBR) used for this test is part of a mobile containerized waste water treatment plant of EnviroChemie. It consists of a biological cleaning part with membrane filtration an active coal filter for post treatment and a reverse osmosis plant with an expansion tank for in- and outflow. The description focusses only on the MBR tests.

Major Components

The MBR is being fed from IBCs into an internal preparation container of the MBR. This container consists of 5 basins with V_{Rk} = 600 L each. Two of the containers are equipped with stirrers to be able to use nitrification and/or denitrification. The focus of the test was on DOC degradation, therefore (de-)nitrification was not used.

Membrane chamber is fed from the last of the reactor cascade. From there the outflow falls back into the basin. The membrane chamber contains hollow fiber membranes (surface A_{Mem} = 23.2 m^2. The reactor cascade is additionally mixed by internal recirculation from the last to the first basin. The following chart shows the design.

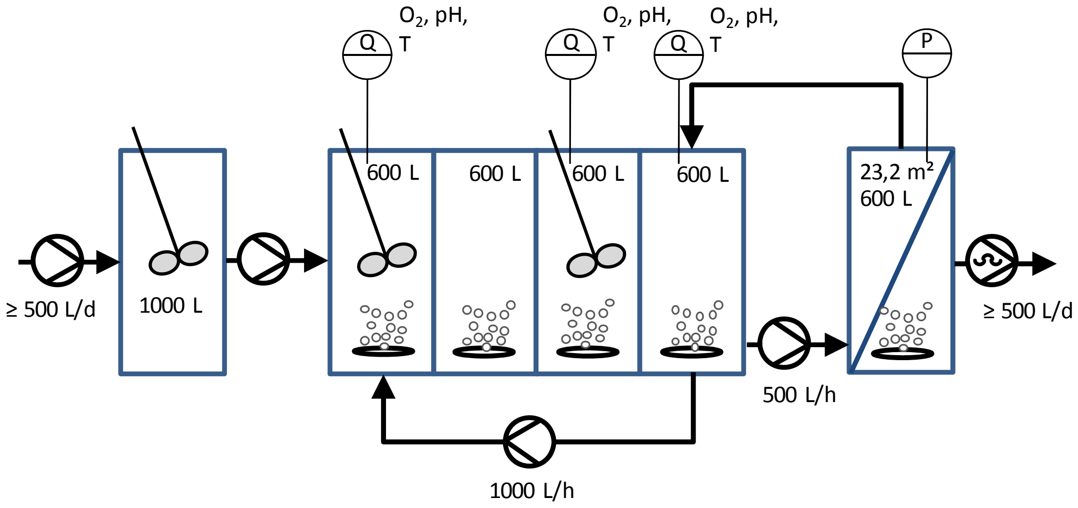


Figure C.8: Process scheme of the MBR plant Biomar® OMB

Instruments and Control

- All aeration tanks have sensors for pH and temperature. In addition oxygen saturation and redox potential are measured.
- The membrane unit has a level-, pressure and throughput measurement.
- The plant can be operated automatically.

C.5.2 Results of Permeate Treatment

C.5.2.1 Runtime and disturbances

The test was done for a period of 30 days continuously. No major disturbances could have been reported.

C.5.2.2 Test facilities and operation

In the beginning, the MBR was feed with a mixture of several types of process waters were filled into the reactor, a total of 3000 liters dm was 5 g/m^3.

After an initial period of 7 days, the inflow was fixed at $Q_d \geq 500$ l/d. This throughput showed only few variations between 545 l/d ± 50 l/d. Variations can be attributed to the slight changes of the permeability of the UF membrane and different runtimes of the filtration pump.

Phosphor was added as watery solution of Natriumdihydrogenphosphate-Dihydrate in the proportion of CSB:P = 200:1. Water hardness was not changed.

Generally, a rapid foam formation occurred in the reactor cascade, but especially in the membrane chamber. Foam shifted over time, but did not disappear during the whole test. Therefore, mechanical foam destroyer have been fixed at the stirrer to prevent an overflow of foam. The membrane chamber was sealed. If needed, biologically degrading foam destroyer was added, max. 3,3 ml/m^3 per day.

C.5.2.3 Degradation of DOC and CSB

In the beginning CSB and DOC concentrations in the outflow increase, due to some dilution effects in the process water used. Beginning with day 19 the outflow concentrations remain relatively constant, CSBe = 1000 mg/l bzw. DOCe = 310 mg/l.

At this point of time the content of the plant was already changed three times (see Figure C.10). Assuming complete mixture of the system, the dilution effect should not appear under real life conditions, due to the long dwell time. The required DOC = 480mg/l for outflow concentration was reached without effort, even less.

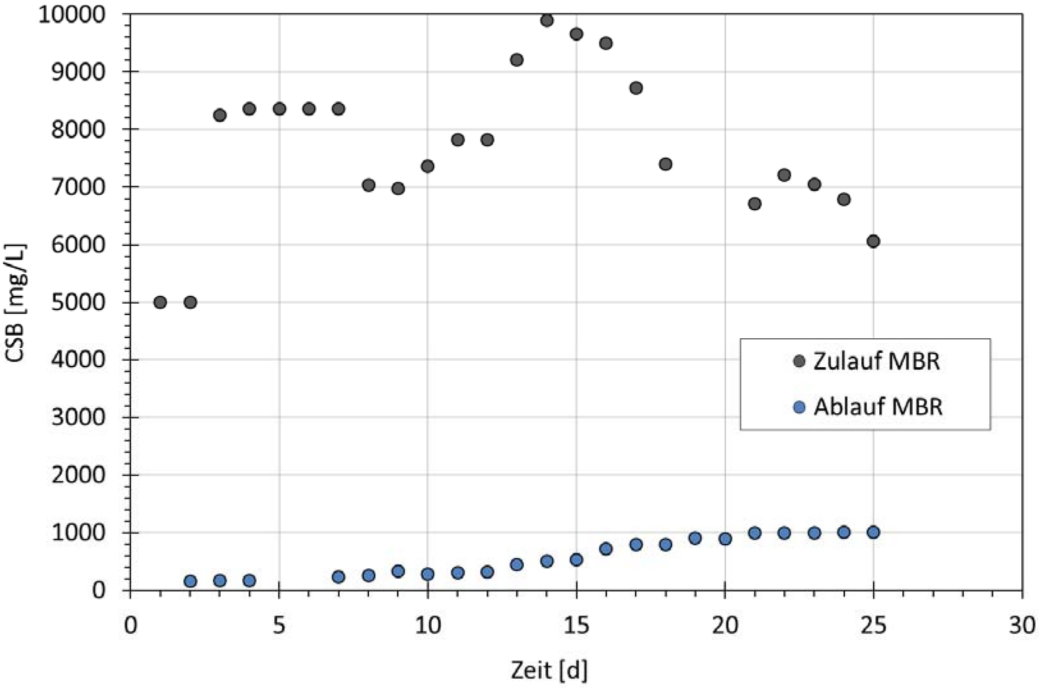


Figure C.9: In- and outflow of CSB

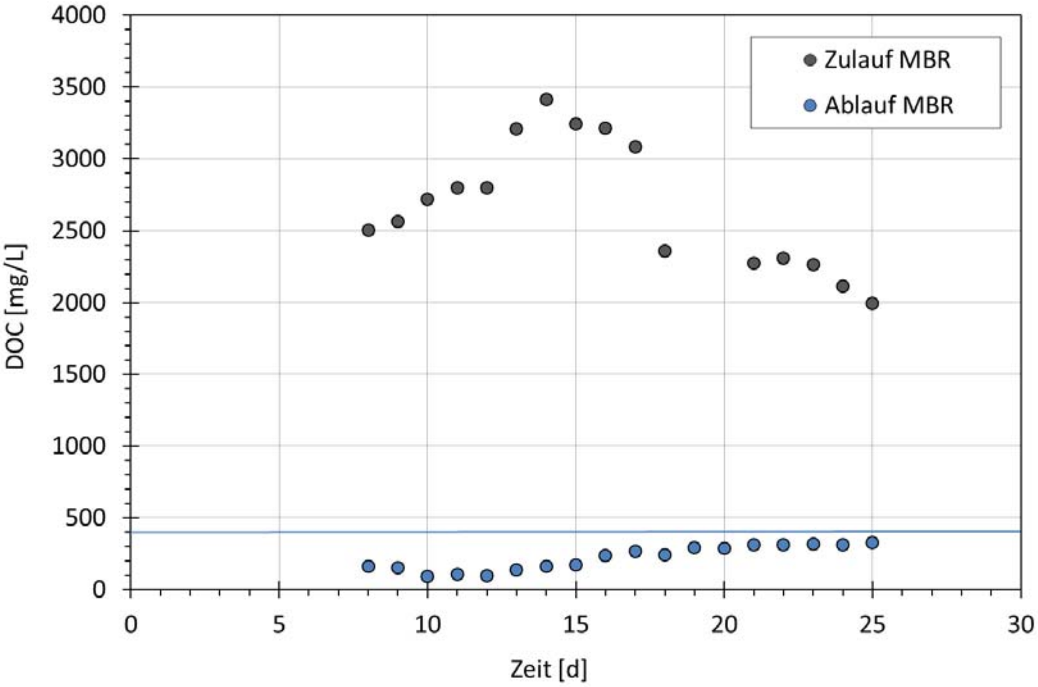


Figure C.10: In- and outflow of DOC

The ratio CSB/DOC as value for the oxidation level of process water is CSB/DOC = 2,9 ± 0,1 on the average. The relation increases insignificantly during the tests.

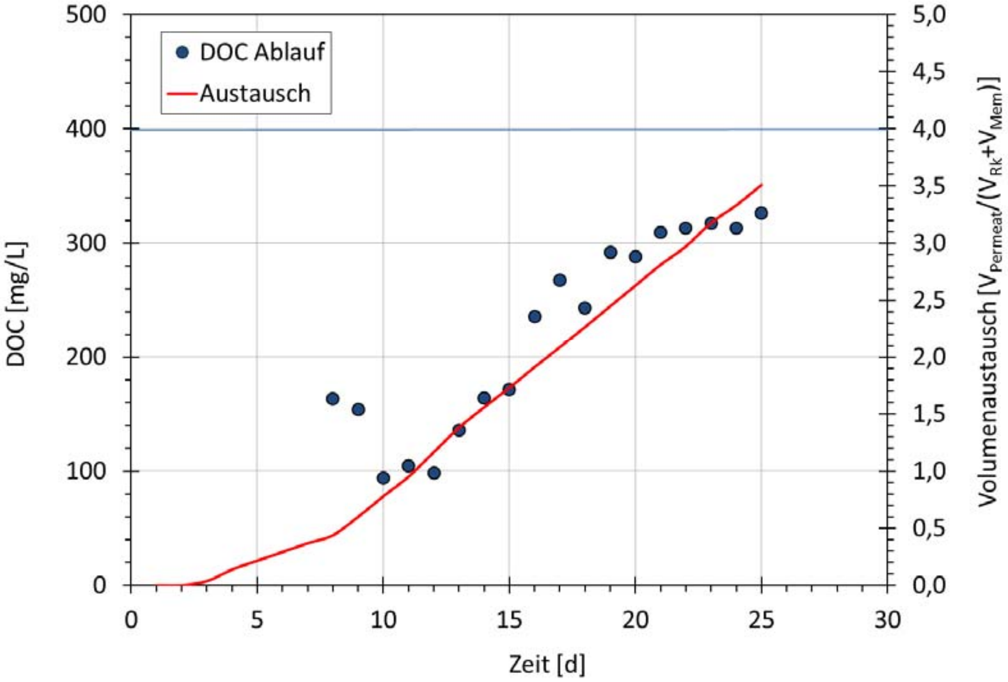


Figure C.11: DOC Outflow (Ablauf) and exchange rate

C.6 CONCLUSIONS

Based on the 2 test scenarios, the following conclusions can be made.

C.6.1 Nanofiltration

- The performance of the membrane largely depends on the biomasses used for the HTC reaction and the catalyst. Modifying the operation process, membrane surface and minimal cleaning cycles can be optimised.
- A combination of different types of membranes seems to be the solution of choice to balance process performance and permeate quality. Surface needed and cleaning cycles can be reduced and operating costs are minimal.

Aerobic Waste Water Treatment

- The best removal results of the HTC permeate can be attributed to the high density of acetic acid as batch catalyst. Use of other catalysts leads to results which are a little worse, but in any case DOC in permeate is eliminated to more than 90% after 48h.
- Results show, that the required levels or purity can be reached without a MBR pre-process. It is possible that there are use cases, where this might be of importance, but generally speaking it is not required, even for permeates out of sewage sludge.

Tests showed that NF works very well and fulfil the legal requirements. The NF plant used is flexible and has a long membrane service life, which leads to low operation costs.

C.6.2 Membrane Bioreactor

By the end of this test period the MBR was run continuously for the whole test period, but a stable process was only reached after several adjustments. DOC in the MBR increased during the test up to 320 mg/l, which is sufficient.

Degradation results of the MBR show that organic compounds can be eliminated by 90%. DOC in process water is eliminated by 100% after 5h. This is also true for mixing of permeate qualities. But with respect to the results of the NF tests, an MBR is not necessary for an HTC plant.

To sum it up: long term tests at technicum sized NF and MBR plants prove, that cleaning process water for the sewage system is not a problem. NF is recommended and would be first choice of AVA-CO2.

C.7 STORAGE AND HANDLING REQUIREMENTS

In this chapter 3 concepts are provided for storage and logistics taking into account particle size, humidity and safety regulations.

Determining factors are particle size and humidity, because they are defined by the use cases. As for safety requirements, only German safety requirements are taken into account. They might differ in other countries.

After drying and converting the biocoal into the final form the coal has to be stored. For most purposes a short term storage is sufficient, and this is the focus of the research done.

C.7.1 Shape of BioCoal

The biocoal produced by AVA-CO2 is converted into three shapes:

- Filter cakes
- Pellets
- Dust

Filter cakes

After the HTC reaction, the coal slurry is being dewatered in a chamber filter press. These filter cakes have a dry matter content of 50-60% and are formed as cakes having a size of ca. 50 x 50cm and a thickness of 2-5cm. During the handling process of unloading the chamber filter press and filling into containers for storage and transportation, these filter cakes usually break into irregular chunks of 10 to 20cm, being 2-5cm thick. These chunks can be stored wet or further dried. The wet chunks are mellow and tend to glue together, whereas the dried chunks (> 90% dry matter) are stiff and keep their form, but have a tendency to detach into dust.

Figure C.12: HTC coal – freshly pressed filter cakes

Since these are the determining factors for storing, dry and wet filter cakes are discussed separately in the following chapters.

Pellets

After drying the HTC coal can be pelletized. The pellets usually have a dry matter content of 93 to 95%, diameter of 7mm and a length of 2cm.

Figure C.13: HTC biocoal pellets

Dust

Dust is produced mainly by the mill drying. Dry matter content usually is within the range of 90 to 98%. The particle sizes of 94 to 99% of the dust are smaller than 90 µm. Handling conditions for dust are special, explosion control measures apply.

Figure C.14: HTC biocoal as dust

Mold Formation

BioCoal produced by hydrothermal carbonisation is a biologically active material. The organic content of the matter is disposable for organisms, due to its dissociation during the conversion process. Therefore, the biocoal has a certain inclination to mold formation, especially if it is wet. Mold formation usually starts after 3-4 days and most times is restricted to the surface, but it is possible that a complete filling gets molded.

To prevent mold formation, an inert gas like nitrogen or other inert gases should be added. For cost reasons, nitrogen gas is recommended.

Figure C.15: HTC biocoal mixture of cake and dust with mold

Several tests with air proof barrels show, that even after 5-6 months, there is no mold formation on the coal.

Figure C.16: HTC biocoal cakes with dried out mold

A third way to avoid molding is drying the biocoal to over 90% dry matter substance. If coal has this high dryness, it is very resistant to mold formation (though there are a few observations of some mold formation, which can be traced back to the influence of splash water or high air humidity).

Drying

If the dewatered coal with a dry matter content of 50 to 50% out of the membrane chamber filter press is being stored at open air, it only dries very slowly. To reach a dry matter content of 80 to 90%, an open air storage of 3 to 4 months is necessary (being influenced by air humidity). During this period, mold formation is normal, but the mold dies after some time and does not survive, when 90% of dryness is reached.

This cheap technology can be used for smaller quantities of coal, if mold formation is not a problem, and there is enough space and time for the process.

Self Heating of stored biocoal

Stored in big bags, the coal might warm up to a temperature of up to 50 °C, while the environmental temperature is only about 20 °C. This process is determined by several factors:

There is an anaerobic biological degradation process going on with the coal and depending on the filling height, the material is cemented inside. Reducing the filling height by 50%, also reduces self heating dramatically. Self heating also is determined by the biomass used.

These factors have to be taken into account for the planning of storage halls.

Storing biocoal in metal barrels (200 l)

Storing biocoal in metal barrels has several advantages, if only small amounts of coal have to be stored. The barrels are inherently stable and need only few ground area. They are stackable, if stored on palettes. They have a rubber band and a spring ring closing, so they can be locked air tight. Therefore inert gas can be used for mold prevention.

This storage concept is not applicable for the industrial use of large quantities of coal.

Figure C.17: HTC coal stored in metal barrels

Inertion

Inert gas is pumped into the barrels by a fitting. Inerted biocoal is absolutely stable and can be stored for a very long period of time. Analyses of many samples of inerted biocoal over a long period could not identify any mold.

Cementing of biocoal

Due to its own weight, biocoal can cement. This especially the case, if the coal is still wet. This phenomenon happens with coal chunks and dust. It does not influence the quality of the coal, but its handling and further processing.

If dried to a dry matter content > 90% the matter remains pourable, and coal chunks do not clump together.

Storing Biocoal in Big Bags

The big bags used at AVA CO2 are made of synthetical textile and have a capacity of 1m^3. They can be covered with an integrated plane, but they cannot be closed tightly. They are not form stable and they cannot be piled.

This packaging is used, if larger volumes of biocoal have to be disposed. Generally, this kind of coal is only dewatered and has a dry matter of 50 to 60%.

It is possible to store coal pellets in big bags, but it has to be taken into account, that they will probably get moldy, even if dry matter content is better than 90%. Air humidity condenses on the surface of the coal, thus enabling molding.

Big bags are not usable for the storage of coal dust due to the textile structure of the bags and the fact, that they cannot be closed.

Figure C.18: HTC coal stored in big bags

Recommendations for large scale storage

Based on these findings some recommendations for large scale storage can be given:

The storing techniques described above work very well within a technicum framework, they cannot be transferred to industry scale. Logistics would be too expensive and extensive, the storing containers too costly. Therefore we recommend to use either bunkers or silos.

From a storage point of view, dry pellets or chunks can be recommended, because they keep pourability even on big scale. Therefore, no forced transportation is required (screw conveyor or a shaker), molding is unlikely to happen.

HTC coal in dust form also is immune against molding, even if stored in an open barrel. But storing and handling requires explosion control, which raises costs. Cementing might happen, which reduces pourability.

We do not recommend storing of wet biocoal. It will mold and cement in all forms.

These recommendations are based on storage and logistics considerations. The form of the biocoal is also determined by the use case (burning plant used and feeding technologies).

Inertion cannot be recommended for large scale storage, because it is too expensive and requires tight bunkers and silos, which further raises costs.

AVA CO2 strongly recommends drying of coal in all forms (dust, pellets, chunks) and short term usage to avoid the problems stated. With short term we mean a period of several days of up to several weeks.

Summary of Storage Tests

The analyzed and tested storage concepts are valid, if small and medium sized of HTC coal of up to several tons of biocoal have to be stored for several weeks or months. For most use cases this should be enough, even under industrial conditions, because usually the coal is produced for immediate combustion. Large volume and long time storing of HTC coals (several 1,000 tons of biocoal stored for more than 6 months) require future analysis. This analysis should have a focus especially on the potential change of biocoal properties in time.

C.8 DRYING TECHNOLOGIES TESTED

After the filtration process, the wet coal is mechanically dewatered using a chamber filter press. This results in a dry matter of 50-60%.

Figure C.19: Chamber filter press at AVA-CO2 Forschung

The dewatered matter is thermally dried, which is necessary for storage, transportation and further usage, be it burning or non-energetic use cases like activation.

Figure C.20: Freshly dewatered HTC biocoal

The following chapters describe the drying technologies analysed and tested. Most of the work was carried out on the premises of AVA-CO2 Forschung GmbH in Karlsruhe, in some cases the plants of suppliers and producers had to be used for logistic reasons. The plants used have been technicum sized plants requiring several batches of drying, because there is no industry sized plant available for the specific requirements of HTC coal.

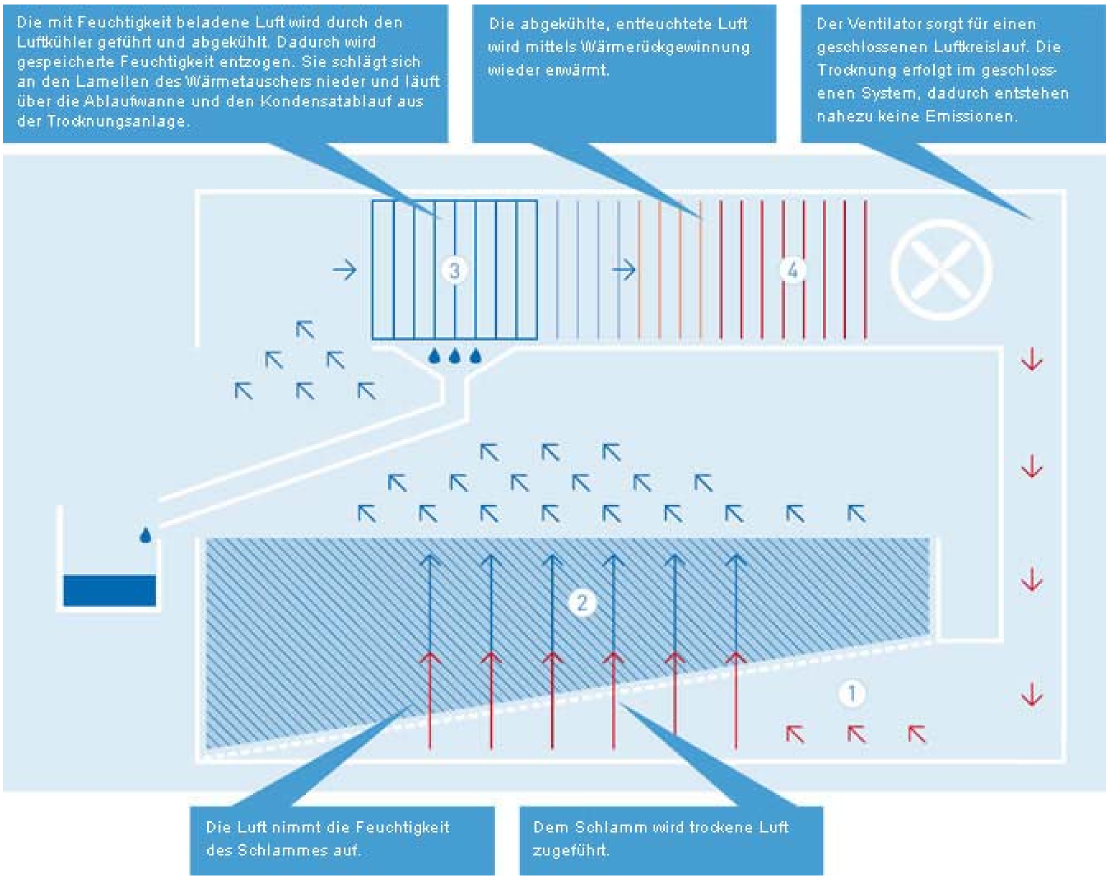
The major target was defined: achieving an HTC coal as dry as possible for each technology. Energy balance was also taking into account, but could not always been measured in an appropriate way.

C.8.1 Technologies used

The technologies used are so called convective trying technologies. HTC coal is very temperature sensitive, the self ignition point being at about 100 °C. Therefore only temperatures between 20 and 80 °C have been used.

C.8.1.1 Cold drying technologies

Dry air drying is a convective drying technology. Air flows through the wet coal, the humidity evaporates and is transported outside the drying chamber. Since the air has a temperature of 40 °C the air has to be dried before it enters the coal chamber in order to increase the humidity absorption capacity. This is done by a low temperature condensation process followed by a warming up step. Ideally, this is done by an integrated heat exchange system. The air is being circulated in a closed system, thus avoiding emissions. The condensate is being turned aside.


Die mit Feuchtigkeit beladene Luft wird durch den Luftkühler geführt und abgekühlt. Dadurch wird gespeicherte Feuchtigkeit entzogen. Sie schlägt sich an den Lamellen des Wärmetauschers nieder und läuft über die Ablaufwanne und den Kondensatablauf aus der Trocknungsanlage.

Die abgekühlte, entfeuchtete Luft wird mittels Wärmerückgewinnung wieder erwärmt.

Der Ventilator sorgt für einen geschlossenen Luftkreislauf. Die Trocknung erfolgt im geschlossenen System, dadurch entstehen nahezu keine Emissionen.

Die Luft nimmt die Feuchtigkeit des Schlammes auf.

Dem Schlamm wird trockene Luft zugeführt.

Figure C.21: Process Scheme of cold air drying (source: Harter Oberflächen- und Umwelttechnik GmbH)

AVA-CO2 used 2 different dryers for BioBoost purposes, one being a continuous chamber dryer and the other being a non-continuous belt dryer.

C.8.2 Non-continuous drying

The basic setup of the non-continuous drying plant is rather simple: it consists of a ventilation system, a reactor through which the air flows and a heat exchange system.

The plant used by AVA-CO2 for BioBoost had the following parameters:

Table C.5: Performance Data of Harter Drymex (manufacturer's data)

Producer/type designation	Harter Drymex M3
Mode of operation	Non-continuous
Performance Capacity	Up to 300 kg per batch
Drying Capacity	250 l in 24 h
Drying Capacity	6 kW

Preparation and Feeding

There have been no special requirements for the preparation of the HTC coal out of the membrane chamber filter press. The HTC coal filter "cakes plates" had to be broken into smaller pieces, the size being between 2 and 20 cm and being 1 to 5 cm thick. After defined time intervals, samples were taken for the analysis of the dry matter achieved. As a general rule it can be stated that a dry matter of up to 97 or even 99% can be reached, depending solely on the retention period of the coal in the chamber.

A major issue that occurred is, that the coal dries very irregularly. Some parts are dryer than other parts. Therefore an average dry matter content was measured using a mixed sample from various parts of the chamber. The following chart shows the drying process.

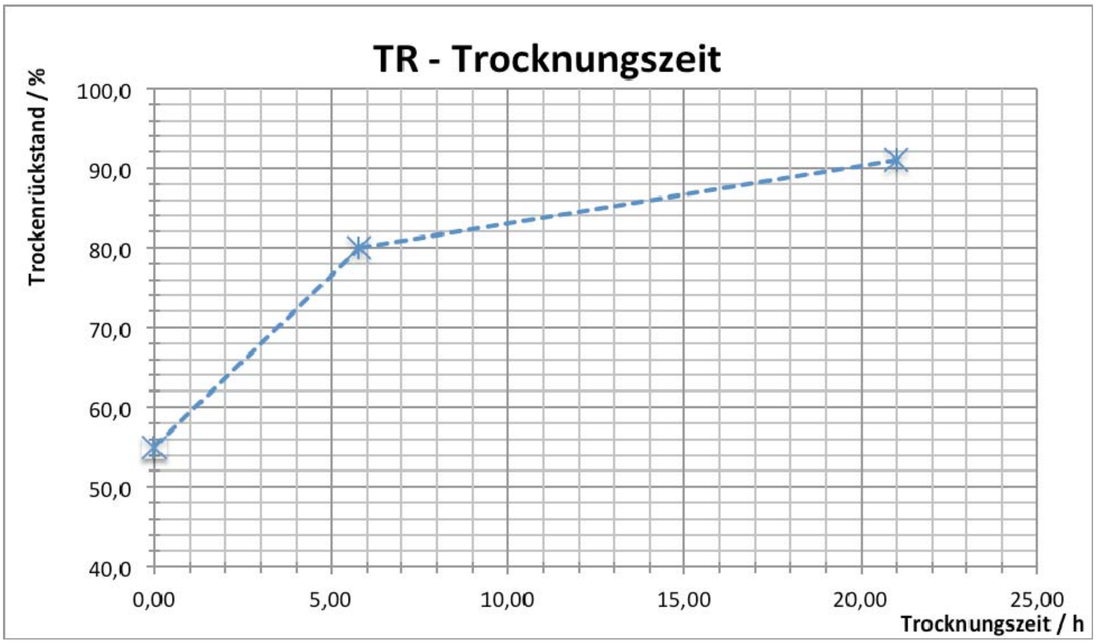


Figure C.22: Typical drying process with a non-continuous cold air dryer

Explanation: in the beginning of the process, the water on the surface of the coal evaporates, while the water from within the coal is transported to the outside. With increasing dryness the evacuation of the inner humidity slows down significantly.

Using different kinds of biocoals and particle sizes, it could be proved that particle size influences the drying period significantly. This can also be related to the biomasses used. Using low compact particles, which is typical for the biocoal produced out of brewery spent grains and organic municipal waste results in a drying performance of 2.2 l/h, compared to sewage sludge which shows a drying performance of 5 l/h (both samples had a dry matter content of about 50% in the beginning). The major reason for this difference is the higher dust content in the chamber, which leads to a higher density of the fill, thus reducing the effectiveness of the air flow. Biocoal particles from biomasses like brewery spent grains and organic municipal waste also show smaller capillaries, which might influence the drying process by a slower transportation flow from the inside of the particles to the outside.

Feasibility of Technology

This technology is very robust and relatively insensitive to dust. It is easy to use and requires no continuous supervision. It is not necessary to standardize the input coal, but of course, the more homogeneous the input is, the better works the drying process.

On the other side, it has to be taken into account, that the matter in the drying chamber is not moved during the process, which leads to long drying periods, if a consistent product with defined qualities must be achieved. This results in significant differences depending on the coal used.

C.8.3 Continuous Drying Technologies

The continuous drying system tested was a belt dryer. The dry air generator is similar to the non-continuous system tested. The speed of the belt and adjustable break periods make it possible to manage the throughput time.

Table C.6: Leistungsdaten Watropur Watromat (manufacturer's data)

Producer/type designation	Watropur Watromat 300B
Mode of operation	continuous
Performance Capacity	Up to 400 kg dry matter per day
Drying Capacity	400 l in 24 h
Drying Capacity	8 kW
Performance	0,3 kW/kg H2O

The dryer is being filled from above through a nozzle and has a capacity of 80kg. The dried material is filled into a bag through a nozzle with a diameter of 10cm.

Preparation and Feeding

It is required, that the material is chopped into pieces of no more than 3 cm. Most particles have been much smaller using a cutting machine.

Doing several batches an optimal residence time and belt speed should have been found out to reach a maximum dry matter. For the adjustment tests of the system, HTC coal from spent brewery grains was used.

Results

Preparatory tests lead to a number of problems, which made it impossible to achieve valid parameters. Some batches of coal could have been dried successfully, but not under stable and reproducible conditions and only after extremely long drying periods.

Some of the problems identified were:

- Even though the material was prepared as required the product outlet was blocked very often, leading to an automatic shut down of the system

- If the filling level of feeding nozzle sank below a defined value, the system stopped automatically. Since AVA-CO2 did not work with night shifts for these tests, it had to be stopped or slowed down extremely.

- There are dust filters implemented in the vent air stream. Due to the chopping of the material during preparation, dust is unavoidable. This dust blocks the dust filters, thus reducing air throughput, which in turn leads to an irregular on/off behaviour of the system. Cleaning the filter takes about 2h and has to be done repeatedly. In addition working with dust requires dust masks for the workers and special protective clothing.

- Due to the minimal air throughput the system is inclined to freezing, which limits a proper operation.

As a result it must be stated, that a regular operation of this system is not possible and cannot be recommended. Not taken into account the excessive manual labor to overcome all kinds of dysfunction, some batches of coal could be produced, dry matter content ranging from 87% to 98%.

The system cannot be used the way it was delivered due to the dust problem in the air stream. This could be avoided if a continuous dust stripper would be implemented (an air cyclone, for example). The few basic performance data we could gather hint at some hidden potential of this technology for drying HTC coal: it could be operated automatically and dryness to be reached can be defined very precisely. But a modification of the plant could not achieved within the time and budget frame given. Therefore, this technology had to be neglected for further investigation.

C.8.4 Mill Drying

Mill drying is a convective technology like the other ones tested. The HTC coal is grinded in a fast rotating mill up to a few µm and blown out by an air stream. This process is basically intended to standardize the matter input, but the air stream can be heated, thus drying the material which is blown out. Due to the fact, that the surface of the matter is increased during the milling process, this technology is very efficient.

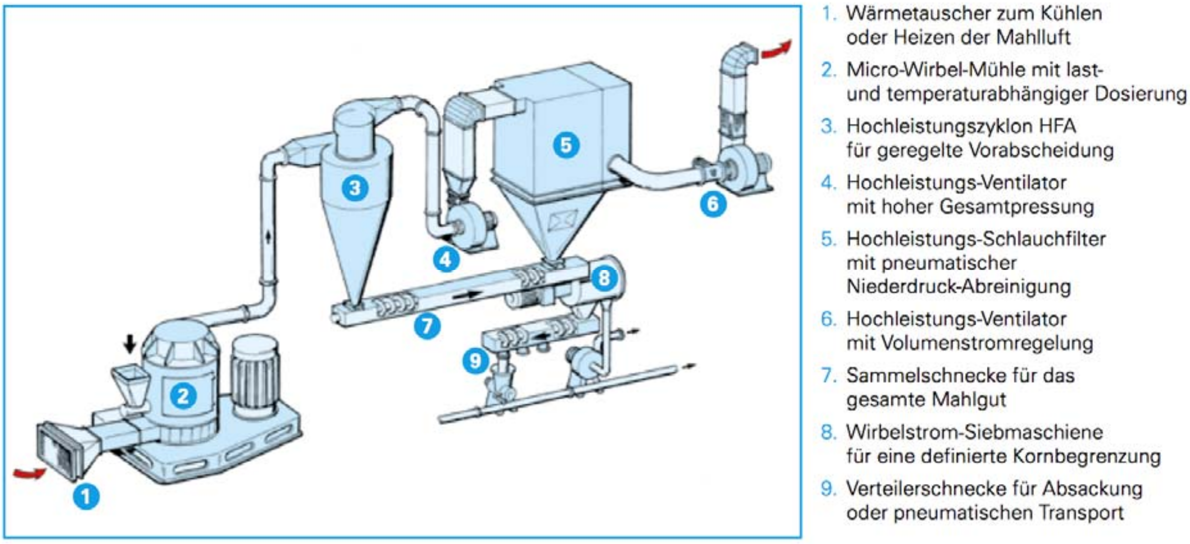


Figure C.23: Mill Dryer plant (Source: Goergens)

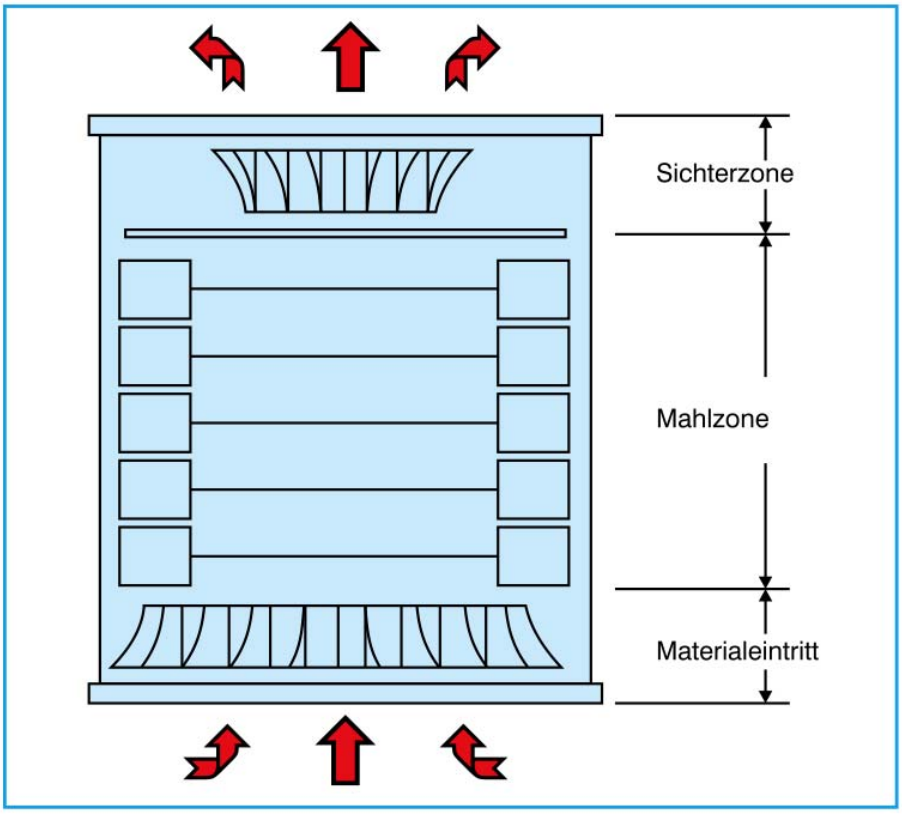


Figure C.24: Schematic scheme of a mil dryer (source: Goergens)

Table C.7: Performance data of a mill dryer (source: Goergens)

Producer/type designation	Mahltechnik Goergens Turborotor G-55
Mode of Operation	continuous
Drying Capacity	Up to 300 kg/h
Drying Capacity	Up to 120 l/h
Performance (el.)	0,01 to 0,1 kW/kg Input
Performance (th.)	1 kW/kg H2O

Preparation and Feeding

Several tests with different kinds of HTC coal have been carried out.

The matter has to grinded to a particle size of ca. 5mm and is transported by a conveying screw into the whirl mill. The matter is milled in the mill and heated up to 40 to 80 °C. After milling and drying the matter is cooled down and collected in bags.

The tests were run on the premises of Goergen. In addition to their test results, AVA-CO2 analysed dry matter content in their own labs.

Table C.5: Leistungsdaten der Mahltrocknung (Versuchsprotokoll)

HTC biocoal	**Horse manure and digestate**[2]	**Sewage sludge**[3]	**Brewery spent grains**	**Organic household waste**
DM in	36,8 %	55,7 %	52,5 %	88,6 %
DM out	95 %	88 %	95,2 %	91,1 – 92,5 %
Buld density in	568 kg/m^3	646 kg/ m^3	611 kg/ m^3	426 kg/ m^3

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[2] Data only for reference (not part of BioBoost tests)

[3] Data only for reference (not part of BioBoost tests)

Bulk density	474 kg/ m^3	654 kg/ m^3	250 kg/ m^3	287 kg/ m^3
Grain Size	94 % < 90 µm	99 % < 90 µm	99 % < 90 µm	97 % < 90 µm
Throughput	66 kg/h	90 kg/h	111 kg/h	Keine Angabe
Temperature	60 °C	46 °C	74 °C	Keine Angabe
Drying Performance	38 l/h	29 l/h	47 l/h	Keine Angabe
Energy need	1,7 kWh/kgTR	0,7 kWh/kgTR	0,9 kWh/kgTR	Keine Angabe

Evaluation

Using mill drying, a very high drying level can be reached. Du to technological restrictions only dust can be achieved, other granularities cannot be produced.

Mill drying is a very efficient technology, dry matter content to be achieved can be managed very precisely by temperature control.

On the other side, handling and storage and further treatment of the HTC coal have to be taken into account, which can result in additional requirements (see below).

One disadvantage is also the high mechanical stress of the material, due to the fast turning rotator. HTC coal with a high ash content will lead to material erosion, which in turn leads to higher maintenance costs.

C.8.5 Solar Drying

Solar drying is a combination of radiation and convective drying. The HTC matter is being warmed up by (infrared) sun rays and the evaporated humidity is being transported by the environmental air.

This technology was used to dry several kinds of HTC coal between 100 and 1,000kg. The wet HTC coal was not prepared especially. It was loosely deployed on several metal plates 2m^2 each.

After 2-3 days up to 90% of dry matter content was reached, depending on the HTC coal.

Of course, this process is extremely cheap in terms of energy costs. Disadvantages are the large surface needed and dependency on the weather. To use this technology in a professional way, covered halls with systematic air circulation would be necessary, which reduces the advantages in energy savings substantially. Drying period is 10 to 15 times longer than any of the other technologies tested, which further limits the usability of this technology.

C.8.6 Comparison of Technologies / Final conclusions

The most important findings are put together in the following table, based on HTC coal out of brewery spent grains and organic municipal waste. This comparison is somewhat limited, because the test plants used had different sizes and prices. However, the analysis provides an insight to feasibility.

Table C.6: Comparison of Technologies / Performance Data

Technology	Drying Performance	Throughput	Energy
Cold air (non-continuous)	2,2 to 5,7 l/h	6,2 to 12,4 kg/h	0,5 to 1,8 kWh/kg DM
Cold air (continuous)	1,2 to 4 l/h	3,3 to 8,3 kg/h	1,7 to 1,9 kWh/kg DM
Mill Drying	29 to 74 l/h	66 to 111 kg/h	0,7 to 1,7 kWh/kg DM
Solar	No data available	No data available	0 kWh/kgD M

Table C.7: Comparison of Technologies, Advantages and Disadvantages

Technology	Advantages	Disadvantages
Cold air (non-continuous)	- robust, low maintenance costs - simple setup - no preparation of matter required	- charge operation - no movement/stirring of matter - inconsistent, irregular drying results
Cold air (continuous)	- continuous operation - dry matter degree adjustable - matter gets moved during drying - simple setup - regular, even drying	- matter must be prepared - susceptible to dust - fine tuning is difficult
Mill Drying	- continuous operation - dry matter content well adjustable - regulbar, even drying - high throughput - high drying performance	- complex setup - preparation of matter required - mechanical stress to plant and product - erosion - not suitable for matter with high portion of sand (sewage sludge) - product is dust
Solar	- low energy need - low labor costs - low maintenance costs - simple setup	- high need of space - dependent on weather - long drying periods

Summary and Recommendation

Each of the technologies tested for BioBoost has specific advantages and disadvantages. Therefore, there is no clear recommendation. It depends largely on specific use cases, the biomasses carbonised and their further treatment after drying.

Within the scope of BioBoost, where organic municipal waste and brewery spent grains are the most promising biomasses for HTC, mill drying is recommended. However, if an HTC plant is co-located with some industry plant (for ex. a brewery), things might change. Therefore, the project specific masterplan defines the parameters for the drying technology to choose.

C.9 SAFETY REQUIREMENTS

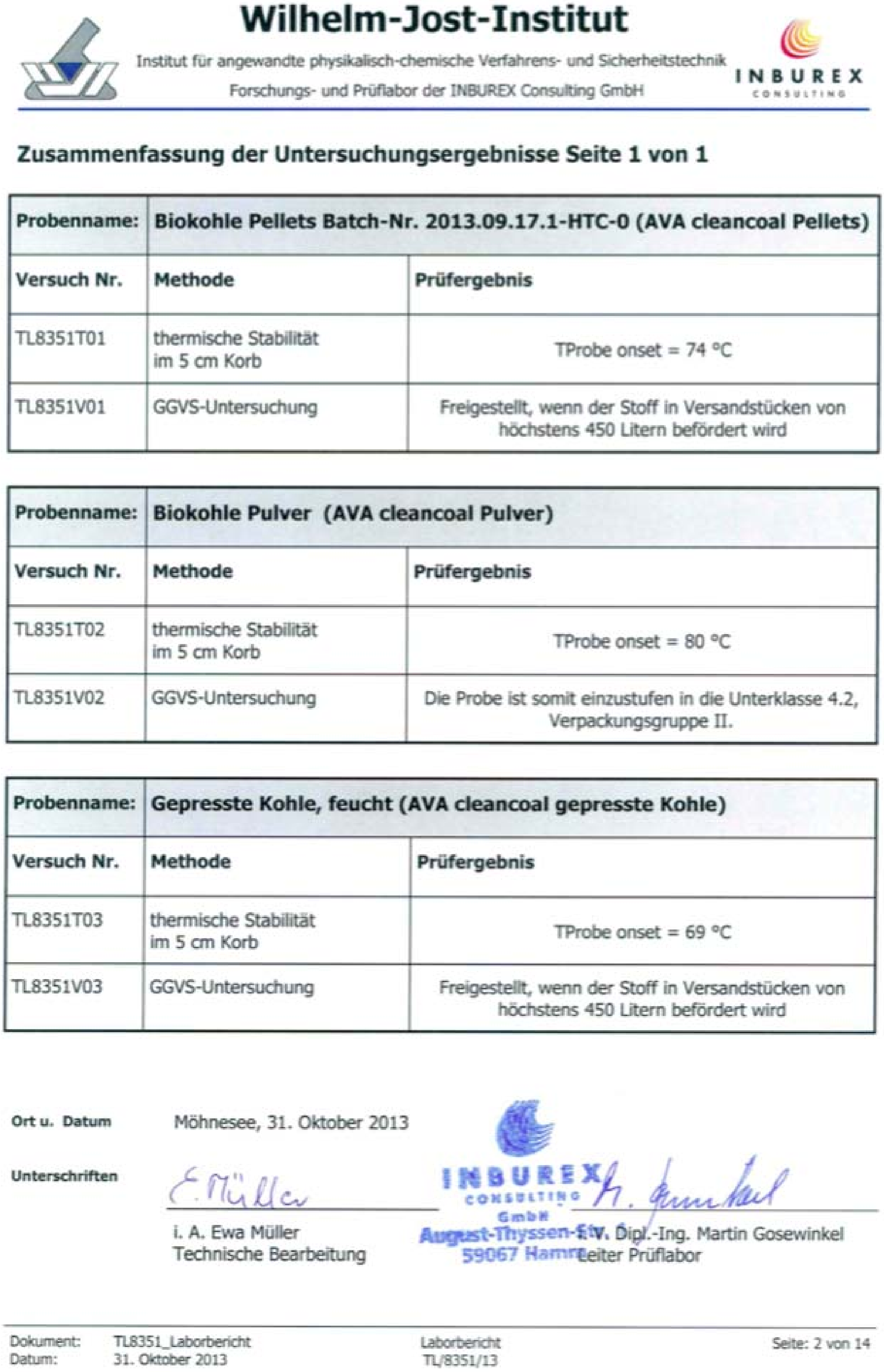
AVA-CO2 has analysed safety requirements together with Wilhelm-Jost-Institut.

The major results are summarized in the following table.

Tests were done with the forms of HTC biocoal discussed in this report: pellets, dust and humid pressed cakes. Several storing tests were done under different conditions in order to find out the self ignition point of HTC biocoal.

Major results:

- HTC coal can be transported in barrels up to 450 l (for pellets and pressed cakes)
- According to the classification for the transportation of hazardous goods, it is categorised in subclass 4.2, packaging group II (for dust)



Wilhelm-Jost-Institut

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Forschungs- und Prüflabor der INBUREX Consulting GmbH

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Zusammenfassung der Untersuchungsergebnisse Seite 1 von 1

Probenname:	**Biokohle Pellets Batch-Nr. 2013.09.17.1-HTC-0 (AVA cleancoal Pellets)**	
Versuch Nr.	**Methode**	**Prüfergebnis**
TL8351T01	thermische Stabilität im 5 cm Korb	TProbe onset = 74 °C
TL8351V01	GGVS-Untersuchung	Freigestellt, wenn der Stoff in Versandstücken von höchstens 450 Litern befördert wird

Probenname:	**Biokohle Pulver (AVA cleancoal Pulver)**	
Versuch Nr.	**Methode**	**Prüfergebnis**
TL8351T02	thermische Stabilität im 5 cm Korb	TProbe onset = 80 °C
TL8351V02	GGVS-Untersuchung	Die Probe ist somit einzustufen in die Unterklasse 4.2, Verpackungsgruppe II.

Probenname:	**Gepresste Kohle, feucht (AVA cleancoal gepresste Kohle)**	
Versuch Nr.	**Methode**	**Prüfergebnis**
TL8351T03	thermische Stabilität im 5 cm Korb	TProbe onset = 69 °C
TL8351V03	GGVS-Untersuchung	Freigestellt, wenn der Stoff in Versandstücken von höchstens 450 Litern befördert wird

Ort u. Datum Möhnesee, 31. Oktober 2013

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TL/8351/13
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Figure C.25: Key figures for safety measures of HTC biocoal