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Biomass based energy intermediates boosting biofuel production

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Deliverable

# **Feedstock selection, Characterization and Preparation**

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## **Publishable Summary**

During the first 9 months of the BioBoost project, different types of biomass have been sourced and characterized as feedstock for energy carrier production by fast pyrolysis (FP), catalytic pyrolysis (CP) and hydrothermal carbonization (HTC). For each technology, at least two biomasses were selected and fully characterized. In addition, straw was characterized by all three technologies. These are the biomasses according to technologies:

### **FP (fast pyrolysis):**

- Middle fraction (residues from flour production)
- Miscanthus
- Scrap wood (industrial residue wood)
- Wheat straw

### **CP (catalytic pyrolysis):**

- Beechwood (commercial wood biomass under the brand name Lignocel)
- Miscanthus
- Wheat straw

### **HTC (hydrothermal carbonization):**

- Organic municipal waste
- Spent grains from breweries
- Wheat straw

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# Report

## 1 Parameters for chemical and physical characterization

For the suitability and assessment of a type of biomass for the various conversion pathways, the characterization of the biomass feedstock is essential.

### 1.1 Molecular structure

From the chemical point of view, biomasses – also called *biogenic solid fuels* – mainly consist of the three bio-polymers cellulose, hemicelluloses and lignin. Other constituents are extractives like fats, resins and ash [1]. Table 1-1 shows the range of composition for different types of biomasses as well as the net calorific values.

Table 1-1: Percentages of bio-polymers and extractives/ashes in biomasses and net calorific values of the constituents cellulose, hemicelluloses, lignin and extractives (from [1]).

	Cellulose (mass-%)	Hemicelluloses (mass-%)	Lignin (mass-%)	extractives/ashes (mass-%)
deciduous wood	40 – 42	30 - 35	20 - 22	2 - 3
coniferous wood	40 – 43	21 - 23	27 - 28	3 - 5
annual plant	38 – 42	25 - 30	15 - 21	5 - 10
Net calorific value (in MJ/kg)	17.3	16.2	27.0	35.9 (extractives only)

**Cellulose** is the major constituent of the cell wall and is responsible for the tensile strength of the biomass. It consists of D-glucose molecules, which are linked via  $\beta$ -(1-4)-bonds to form a branchless polysaccharide (see Figure 1-1). The degree of polymerization and the chain length varies and can contain – depending on the kind of biomass – up to 14000 monomers [1].

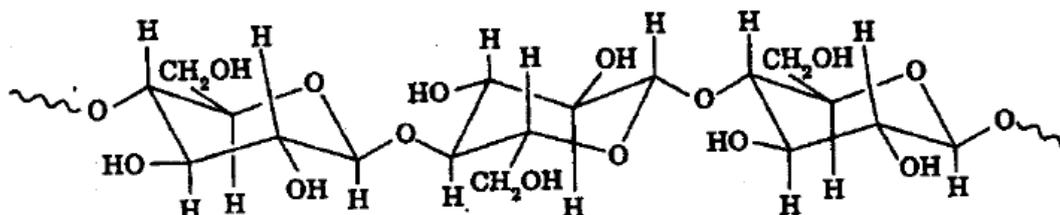


Figure 1-1: Chemical structure of cellulose (from [2]).

**Hemicellulose** is the collective term for branched polysaccharides consisting from different monomers. Monomers are amongst others hexoses (glucose, mannose, galactose), and pentoses (arabinose, xylose). Because of the great variety of compounds, an absolute structural formula cannot be given. Figure 1-2 shows just an example of a part of a possible compound. Hemicelluloses have various functions in the plant, e.g. supporting cell membranes, reserve material and adhesive [1].

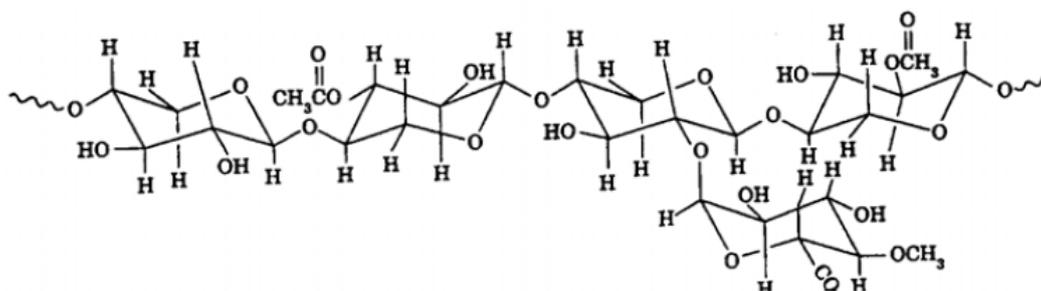


Figure 1-2: Example of a part of the chemical structure of hemicelluloses (from [2]).

**Lignin** is the third main component, not being an independent but a supporting component for cellulose. Its putty and stiffening effect results in the high stability of wood. Lignin is a highly complex, three-dimensional cross-linked polymer compound with a propyl-benzene-structure. Figure 1-3 illustrates just a small section of a lignin polymer, featuring some typical linkages seen in lignin.

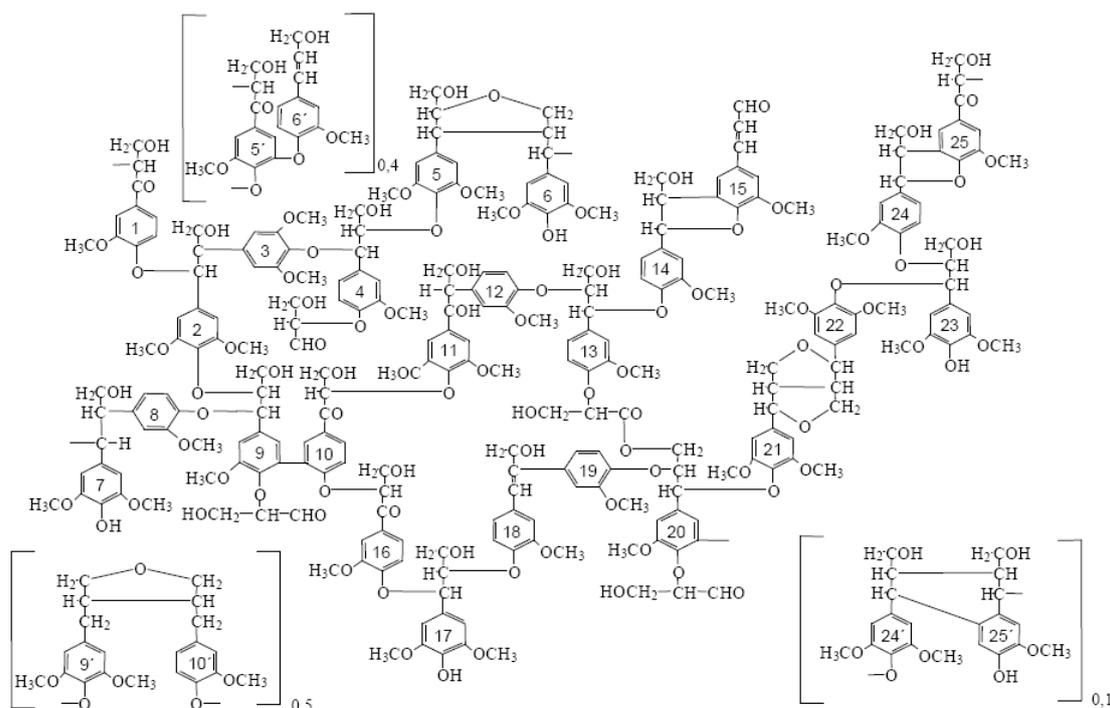


Figure 1-3: Chemical structure of a lignin from beech wood (from [3]).

The percentage of carbon in lignin (about 64 %) is clearly higher than in cellulose (ca. 42 %). Thus, differences in the macro-molecular constitution of biomasses result in different carbon contents, implying different energy contents as the percentage of carbon has the major impact on the calorific value (see chapter 1.5).

Higher percentages of lignin and extractives enhance the calorific value because of their high carbon content [1]. The net calorific values of the different bio-polymers and of the extractives are shown in Table 1-1.

## 1.2 Elemental composition

From all naturally occurring elements on earth, 26 are considered as being biologically relevant for the plants. A distinction is made between main elements (carbon, hydrogen, oxygen), main nutrients (nitrogen, potassium, calcium, magnesium, phosphorous, sulphur) and trace minerals (chlorine, silica, sodium, iron).

Table 1-2: Main elemental composition of fossil fuels (coals) and different biomasses (related to the dry matter), (from [4],[5]).

Fuel/Biomass	C	H	O	N	K	Ca	Mg	P	S	Cl
(mass-% of dry matter)										
<b>coals</b>										
black coal	72.5	5.6	11.1	1.3					0.94	<0.13
brown coal	65.9	4.9	23.0	0.7					0.39	<0.1
<b>woods</b>										
spruce wood (with bark)	49.8	6.3	43.2	0.13	0.13	0.70	0.08	0.03	0.015	0.005
beech wood (with bark)	47.9	6.2	45.2	0.22	0.015	0.29	0.04	0.04	0.015	0.006
poplar wood (short rotation)	47.5	6.2	44.1	0.42	0.35	0.51	0.05	0.10	0.031	0.004
<b>stalky biomasses</b>										
maize stover	45.7	5.3	41.7	0.65					0.12	0.35
wheat (whole plant)	45.2	6.4	42.9	1.41	0.71	0.21	0.12	0.24	0.12	0.09
wheat grain	43.6	6.5	44.9	2.28	0.46	0.05	0.13	0.39	0.12	0.04
wheat straw	45.6	5.8	42.4	0.48	1.01	0.31	0.10	0.10	0.082	0.19
rape grain	60.5	7.2	23.8	3.94					0.10	
rape straw	47.1	5.9	40.0	0.84	0.79	1.70	0.22	0.13	0.27	0.47
grass cuttings (near road)	37.1	5.1	33.2	1.49	1.30	2.38	0.63	0.19	0.19	0.88

Wood fuels have higher carbon content (47 - 50 %) than non-woody fuels (ca. 45 %) because of the lower ash content. The oxygen content varies between 40 and 45 % and the hydrogen content between 5 and 7 % (all mass-related to dry matter). Compared to coals (black, brown and charcoal) – which are formed by coalification – in biomass, the carbon is present in a partially-oxygenated form with relatively high oxygen content. This is the reason for the lower calorific values of biomasses in relation to those of coals (compare Table 1-3). Solid biomass is the initial source for the solid fossil energy carriers. Their grade of coalification can be derived from the elemental composition along the sequence biomass - peat - brown coal - black coal - anthracite.

## 1.3 Water content

The water content  $w$  is defined as the ratio of the mass of water in the biomass related to the total mass of biomass including water, see equation (1-1).

$$w = \frac{m_w}{m_{B,wf} + m_w} = \frac{u}{1 + u} \quad (1-1)$$

Take note not to confuse the water content  $w$  with the fuel moisture  $u$ . The last one is related to the dry matter. The moisture  $u$  is defined as the water mass  $m_w$  contained in the fuel related to the dry mass (water-free,  $wf$ ) of the biomass  $m_{B,wf}$ , see equation (1-2).

$$u = \frac{m_w}{m_{B,wf}} = \frac{w}{1-w} \quad (1-2)$$

The water content of biomass is of great importance for the energetic use. Generally, a high water content (e.g. more than 40 % for freshly harvested lumber) is prejudicial for most thermal process, as the water has to be evaporated from the fuel before or during the process. Due to the high evaporation enthalpy of water this drying process is energy intense. The water content varies strongly for different kinds of biomass as well for the time span between the harvest of biomass and its energetic utilization.

The water content affects substantially the calorific value of a biogenic solid fuel. Water contents between 12 and 20 % for air-dry wood and straw are well-known from practical experience; their net calorific value varies between 16.5 and 19 MJ/kg [6].

The water content is determined experimentally by drying a sample in a dryer at 105 °C until constancy of the mass (according to DIN CEN/TS 14 774). It has to be mentioned that untreated biomass fuels can contain small amounts of volatile, energy-rich substances (extractives). These compounds can escape during drying at 105 °C and thus lead to errors in the determination of the water content. Compared to a drying temperature of 80 °C, the error in the water content has been found to be clearly less than 1 % and therefore is – in most cases – negligible for calorific value assessments. Only for oily materials (e.g. rape oilcake) the error can become more significant [1].

## 1.4 Ash content and composition

The inorganic residue remaining after burning a solid fuel is called *ash*. It originates directly from the fuel (mineral components) as well as from inorganic contaminations during the chain of supply (e.g. during harvesting, processing, transportation, storage).

Ash contains many of the elements listed in table 1-2. It mainly consists of calcium, magnesium, potassium, phosphorous and sodium. For example, the average composition of ash from woody biomass is 42 % CaO, 6 % K<sub>2</sub>O, 3 % P<sub>2</sub>O<sub>5</sub> and 1 % Na<sub>2</sub>O as well as small amounts of iron and manganese. For ashes of straw/stover and whole crop-plants the portions of K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> are higher [1].

The ash content  $a_{wf}$  of dry fuel is defined as the mass of ash  $m_a$  related to the total mass of dry fuel  $m_{B,wf}$ :

$$a_{wf} = \frac{m_a}{m_{B,wf}} \quad (1-1)$$

The ash content of a fuel affects the environmental pollution (emission of contaminants) and the technical design of a processing plant (e.g. gasifier or furnace). Higher ash contents result in higher effort in dedusting techniques, cleaning of (heat exchanger) surfaces, further processing/disposal of the residues etc. [1]. Special consideration is necessary when dealing with thermo-chemical processes (e.g. gasification) using biomass as a feedstock. Problems in these applications can arise from low deformation/melting temperatures of biomass ashes, which can result in sintering and agglomeration (slugging), leading to failure of the plant. The

ash deformation/melting temperatures vary heavily for different biomasses as their elemental composition differs. For straw from crops, the ash deformation temperature can be as low as 700 °C whereas it normally is higher than 1000 °C for woody biomasses [6].

The ash content of biogenic fuels varies in a great range. Wood (including bark) has an average ash content of less than 1 % related to the dry matter. In contrast to this, straw biomass normally has ash contents of more than 4 % of the dry matter [1].

The ash content of a sample is determined by heating it up under defined conditions and measuring the remaining mass. According to DIN CEN/TS 14775, the oven temperature is increased steadily (in an air atmosphere) during a time span of 50 minutes until it reaches 250 °C. This temperature level is kept constant for 60 minutes in order that the volatiles can escape from the sample before burning. Subsequently, the temperature of the furnace is increased steadily at a heating rate of 5 K/min to a temperature of 550 °C. This temperature level is kept constant for at least 120 min. Older measuring instructions (e.g. DIN 51719) advised a clearly higher end temperature of 815 °C. This can result in differences in ash content values from past measurements, which can be explained by the loss of volatile inorganic compounds and further oxidation of inorganic compounds. Depending on the kind of fuel and the level of ash content, this systematic deviation can account to several percentages [1].

## 1.5 Net and gross calorific value

*Net calorific value:* The net calorific value  $H_U$  (or lower heating value,  $LHV$ ) is defined as the amount of heat that is released during complete oxidation of a fuel *without* recovery of the heat of condensation of the water vapor in the exhaust gas.

*Gross calorific value:* In contrast to this, the gross calorific value  $H_O$  (or higher heating value,  $HHV$ ) is defined as the heat released during complete oxidation of a fuel *including* the heat of condensation of the water vapor present in the exhaust gas. In this case, the exhaust gases have to be cooled down to the reference temperature of 25 °C. Compared to the net calorific value, the heat energy recovered is enhanced under these conditions [1].

*Difference:* The water vapor arising during a combustion comes from the reaction of hydrogen present in the fuel with oxygen on the one hand and on the other hand from the free and bound water in the fuel (water content), see equation (1-4) [1].

$$H_U = H_O - r \cdot (w + w_H) \quad (1-4)$$

With:  $H_U$  = Net calorific value of the fuel, crude/moist (kJ/kg fuel)  
 $H_O$  = Gross calorific value of the fuel, crude/moist (kJ/kg fuel)  
 $r$  = specific evaporation enthalpy of water (2443 kJ/kg H<sub>2</sub>O at 25 °C)  
 $w$  = water content of the fuel (see eq. (1-1)) (kg H<sub>2</sub>O/kg fuel)  
 $w_H$  = water fraction of water formed from hydrogen in the fuel during the combustion reaction (kg H<sub>2</sub>O/kg fuel)

- For the water (free or bound) in the biomass, the heat of condensation for each percentage of water content accounts to 2443 kJ per 1 kg fuel (at 25 °C).
- Each mass-percentage of hydrogen in the dry matter of the fuel results in a heat of condensation of 8.936x2443 kJ per 1 kg fuel = 21831 kJ per 1 kg fuel (at 25 °C); (as

from 1 mol of hydrogen H, 0.5 mol of water H<sub>2</sub>O can be formed → 1 kg of H results in 8.936 kg H<sub>2</sub>O).

Thus, knowing the chemical composition (hydrogen content) and the water content of the fuel, the deviation between net and gross calorific value can be calculated [7]:

$$H_U = H_O - r \cdot w - r \cdot 9 \cdot h_{wf} \cdot (1 - w) \quad (1-2)$$

$$H_U = H_O - 2443 \cdot w - 21831 \cdot h_{wf} \cdot (1 - w)$$

$h_{wf}$  is the mass fraction of hydrogen in the water-free fuel (kg H/kg fuel<sub>wf</sub>).

The gross calorific value  $H_O$  of solid biogenic fuels in average is about 6 % (bark), 7 % (wood) and 7.5 % (stalky biomass) higher than the net calorific value  $H_U$ . This holds only for dry solid fuels. For moist biomass, the relative difference becomes bigger with increasing water contents [1], see Figure 1-4.

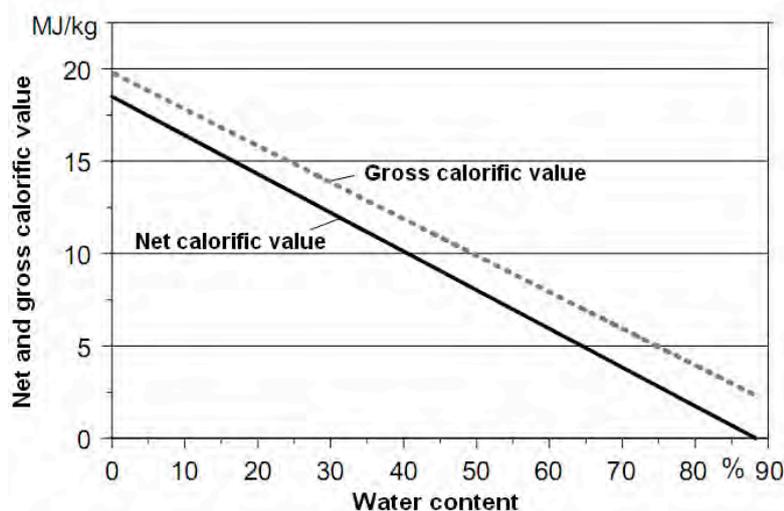


Figure 1-4: Difference between net and gross calorific value at different levels of water content (from [1], modified).

Calculation of the gross calorific value of the crude/moist fuel  $H_O$  from the gross calorific value of the water-free fuel  $H_{O,wf}$ . The actual amount of energy stored in a fuel is characterized by the gross calorific value of the dry substance  $H_{O,wf}$ . Generally, in literature, the values for the gross calorific value are given for the dry substance as  $H_{O,wf}$ . From this value, the amount of energy present in a fuel at process conditions  $H_O$  can be calculated knowing the appropriate water content  $w$  [7].

$$H_O = H_{O,wf} \cdot (1 - w) \quad (1-6)$$

Calculation of the net calorific value of the crude/moist fuel  $H_U$  from the gross calorific value of the water-free fuel  $H_{O,wf}$ . In order to calculate the net calorific value of the fuel  $H_U$ , equation (1-7) can be used when the gross calorific value of the water-free fuel  $H_{O,wf}$ , the water content  $w$  and its hydrogen content  $h_{wf}$  are known.

From equations (1-5) and (1-6) results:

$$H_U = H_{O,wf} \cdot (1 - w) - 2443 \cdot w - 21831 \cdot h_{wf} \cdot (1 - w) \quad (1-7)$$

In practice, the hydrogen content of the fuel often is unknown (e.g. if no elemental analysis is available). In this case, according to [8], an estimation of the hydrogen content in the water-free substance can be done using the ash content of the sample. It has been shown that the values of  $H_U$  calculated with the estimated values for the hydrogen content are about 1 % to 7 % above those calculated with the help of the elemental analysis [7]. The estimation equation (1-8) is shown below:

$$h_{wf} = \frac{(1 - a_{wf})}{15} \quad (1-8)$$

where:  $h_{wf}$  = mass fraction of the hydrogen in the water-free fuel (kg H/kg fuel<sub>wf</sub>)

$a_{wf}$  = mass fraction of the ash content in the water-free fuel (kg ash/kg fuel<sub>wf</sub>)

*Calculation of the net calorific value of the crude/moist fuel  $H_U$  from the net calorific value of the water-free fuel  $H_{U,wf}$  [1]:*

$$H_U = \frac{H_{U,wf}(100 - w) - 2.443w}{100} \quad (1-9)$$

$H_{U,wf}$  is the net calorific value of absolutely water-free biomass (in MJ/kg);  $w$  is the water content (in mass-%) at which  $H_U$  shall be calculated.

*Influence of the ash content:* In addition to the water content, the calorific value is also influenced by the ash content of the fuel, see Figure 1-5. From the diagram, it becomes evident, that for woody biomass, the influence of the ash content on the energy content of the fuel is much less than for stalky biomass (straw, stover, grass) due to the fact, that woody biomasses have much lower ash contents [1].

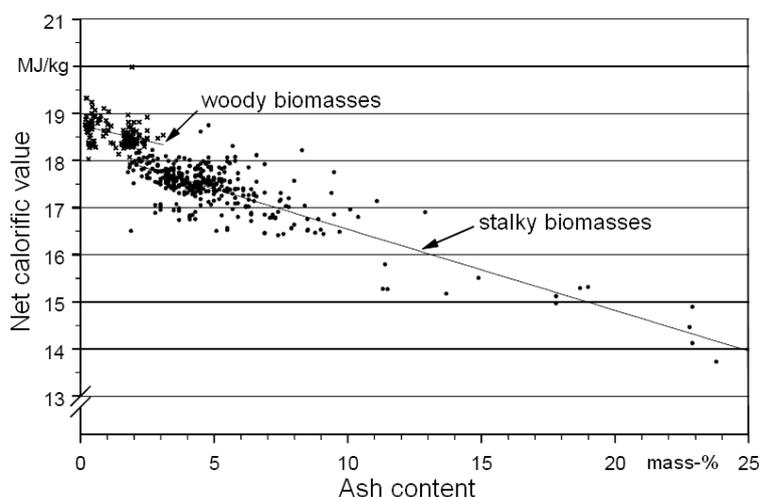


Figure 1-5: Influence of the ash content (water-free base) of woody and stalky biogenic fuels on the net calorific value (as per [9], from [1], modified).

*Estimation methods:* The calorific value of dry solid biomasses is mainly influenced by the content of the elements carbon and hydrogen, which can be oxidized. Furthermore, also the oxidation of some nutrients (e.g. sulphur and nitrogen) releases heat. On the contrary, the oxygen content in the fuel lowers the calorific value because oxidizable compounds that are bound in oxygen-containing molecules are difficult to oxidize to a higher oxidation stage [1]. Thus, the gross calorific value of a fuel with known elemental composition can be estimated by calculation. The approximate formula of *Channiwala* – which can be used for biogenic fuels because of its relatively low mean error of about 4-1.5 % – is shown in equation (1-10) [9]:

$$H_{O, wf} = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211a_{wf} \quad (1-10)$$

The letters C, H, S, N, O and  $a_{wf}$  represent the mass percentages of carbon, hydrogen, sulphur, nitrogen, oxygen and ash;  $H_{O, wf}$  is the gross calorific value in dry state of the fuel in MJ/kg.

Table 1-3 shows the calorific values, ash content and ash deformation temperature for different solid fuels. It is evident that stalky biomasses in average have a lower calorific value than woody biomasses; the difference amounts to ca. 9 %. There is no big difference between straw and grain from crops. Though, for oil fruits (like the seeds of rape plants) there is a notable difference in the calorific value between seeds and straw. This is due to the relatively high value for  $H_u$  of the rape oil of about 36 MJ/kg.

*Table 1-3: Important fuel data; all related to dry fuels (from [4], [5]).*

<b>Fuel/Biomass</b>	<b>Net calorific value <math>H_{U, wf}</math> in MJ/kg</b>	<b>Gross calorific value <math>H_{O, wf}</math> in MJ/kg</b>	<b>Ash content <math>a_{wf}</math> in %</b>	<b>Ash deformation temperature in °C</b>
		<b>coals</b>		
black coal	29.7		8.3	1250
brown coal	20.6		5.1	1050
		<b>woods</b>		
spruce wood (with bark)	18.8	20.2	0.6	1426
beech wood (with bark)	18.4	19.7	0.4	
poplar wood (short rotation)	18.5	19.8	1.8	1335
		<b>stalky biomasses</b>		
maize stover	17.7	18.9	6.7	1050
wheat (hole plant)	17.1	18.7	4.1	977
wheat grain	17.0	18.4	2.7	687
wheat straw	17.2	18.5	5.7	998
rape grain	26.5		4.6	
rape straw	17.1	18.1	6.2	1273
grass cuttings (near road)	14.1	15.2	23.1	1200

*Determination method:* The experimental determination of the gross calorific value  $H_O$  – from which the net value can be calculated later on – is performed by a calorimetric procedure (DIN CEN/TS 14 918). It consists of two separate investigations: burning of a reference substance and burning of the fuel sample at the same experimental conditions. For the determination of  $H_O$  a quantitative combustion reaction in pure oxygen and high pressure is performed so that the products from the combustion are in a defined state. The combustion process takes place in a closed system, the so-called bomb, which is surrounded by a water

bath at about 25 °C; together they make the bomb calorimeter. The change in temperature of the water bath due to the heat of combustion of the sample is measured and thus the gross calorific value can be calculated [1].

## 2 Feedstock selection for the Fast Pyrolysis (FP) at KIT

For the fast pyrolysis performed at KIT, biogenic residues and organic waste materials with low competition in the usage shall be tested as feedstock.

### 2.1 Requirements for fast pyrolysis feedstock

Feedstocks for fast pyrolysis process should have a water content of less than 15 mass-% in order to ensure a high energy efficiency of the process and high product quality, i.e. low water content of the pyrolysis oil [11].

Depending on the application of the products from the fast pyrolysis, the ash content can be a limiting factor. The amount of ash present in the feedstock affects the mass yields of the product fractions gas, pyrolysis oil and char. Higher ash contents lead to lower yields of pyrolysis oil [12], [13].

*Pre-treatment:* The pre-treatment (drying, separation of impurities and grinding) of the feedstock prior to the pyrolysis process should be processable in an easy way. For an efficient usage in a fast pyrolysis plant, it may be necessary to dry the feedstock in order to reduce its water content. For drying, several options are possible, e.g. the usage of sun energy, the usage of waste heat from other process steps and/or by burning pyrolysis gas. The removal of impurities like stones and metal pieces might be necessary for preventing the subsequent apparatuses (grinding, feeding screws, reactor) from damages. This could be done with stone and magnet separators and visual inspection. The grinding of the feedstock to a size of about 5 mm is crucial for having a homogenous feed into the reactor and to realize a sufficient heat transfer from the heat carrier to the biomass particles. The size reduction of the feedstock can be realized by the help of a shredder followed by a cutting mill.

### 2.2 Selection of feedstocks for the fast pyrolysis

Four feedstocks are chosen to be further investigated for the fast pyrolysis process. The selected feedstocks comply with the criteria stated in the previous section. The feedstocks to be investigated are wheat straw, miscanthus, scrap wood and residues from flour production. These materials are further described below.

### 2.2.1 Wheat straw

Wheat straw is an agricultural residue arising from the harvest of wheat grain. The material was delivered air-dry in form of bales. Figure 2-1 shows some stalks of straw making up the bales.



*Figure 2-1: Wheat straw.*

### 2.2.2 Miscanthus

Miscanthus is a perennial crop cultivated for energetic use. The samples were delivered as air-dry straw and grinded.



*Figure 2-2: Miscanthus straw, grinded.*

### 2.2.3 Scrap wood

Scrap wood can be classified as an urban and industrial residue wood. It arises wherever wood is deposited after its actual usage. The scrap wood used belongs to category A2 of the German “Altholzverordnung”. That means: glue-laminated, varnished, laminated or otherwise treated scrap wood without halogen-organic compounds in the varnish and without preserver; wood-based materials without harmful contaminations. The material comprises e.g. packaging and pallets, from construction (demolition, construction zones), furniture etc. The delivered material consists of parts of chipboard and veneer. It was delivered chopped and air-dry and contains plastic, glass and metal parts which have to be separated. Figure 2-3 exemplarily shows the scrap wood used with impurities.



*Figure 2-3: Scrap wood of category A2 as delivered.*

### **2.2.4 Residues from flour production**

From the industrial production of flour in a mill, residues separated by a pneumatic separator are used. The so-called “middle fraction” consists of small and light kernels, kernels with husks and light plant parts harvested, see Figure 2-4. The material was delivered air-dry. Due to the presumably low occurrence of this feedstock, the residues from the flour mill are used as an extra feedstock. The assessment of its potential (within WP1) might be done just for some case study regions, as mill sites and production volumes would have to be investigated manually.



*Figure 2-4: Middle fraction of a flour mill.*

## **2.3 Characterization of the feedstocks**

All air-dry feedstocks were separated from impurities and then cut to particles with a diameter smaller 5 mm with the help of a shredder and a cutting-mill.

### **2.3.1 Analysis Methods**

Samples of the pre-treated feedstocks were analyzed in the KIT laboratories as well as in an external one. In Tables 2-1a&b, the parameters and the corresponding standards and instruments are shown for internal and external analyses, respectively.

Table 2-1a: KIT-internal analyses: Measuring parameters and their corresponding methods.

KIT-internal analyses			
Parameter	DIN/EN Standard	Instrument	Further information
Water content	DIN CEN/TS 14 774-3	LECO TGA 701	original sample, moist, not pre-dried; all parameters are measured in one procedure
Ash content at 550°C	DIN CEN/TS 14775	LECO TGA 701	
Ash content at 815°C	DIN 51719	LECO TGA 701	
Gross calorific value (HHV)	DIN CEN/TS 14918	IIKA C5000 control	cryo-milled original material, no pre-drying, water content corresponds to original sample
Thermogravimetric determination	-	Netzsch STA 409	original sample, moist, not pre-dried
Analysis moisture	DIN 51718	LECO TGA 701	Water content at the time of analysis, cryo-milled powder is dried, afterwards open storage in conditioning box, AF is determined parallel to elementary analysis
Nitrogen content (elementary analysis)	DIN CEN/TS 15104	Elementar Vario EL III / LecoTruspec CHN	Water content corresponds to analysis moisture (cryo-milled powder is dried, afterwards open storage in conditioning box)
Carbon content (elementary analysis)	DIN CEN/TS 15104	Elementar Vario EL III / LecoTruspec CHN	
Sulphur content (elementary analysis)	-	Elementar Vario EL III / LecoTruspec CHN	
Hydrogen content (elementary analysis)	DIN CEN/TS 15104	Elementar Vario EL III / LecoTruspec CHN	
Oxygen content (by difference)	-	-	
			Oxygen content calculated by difference to 100 %

Table 2-1b: KIT-external analyses: Measuring parameters and their corresponding methods.

KIT-external analyses			
Parameter	DIN/EN Standard	Instrument	Further information
Volatiles	DIN EN 15148		
Content of Cl and S	DIN CEN/TS 15289		
Chemical composition of fuel ashes (and slags) (Si, Al, Fe, Ca, Mg, Na, K, Ti, P - as oxides)	DIN 51729, part 1, part 11		
Micro-wave disintegration for subsequent determination of trace compounds	DIN 22022-1		
Content of trace compounds via ICP-OES	DIN 22022-2		
Content of trace compounds, interpretation and results	DIN 22022-6		
Determination of 62 elements via ICP-MS	DIN EN ISO 17294-2 (E 29)		
Determination of selected elements via ICP-OES	DIN EN ISO 11885 (E 22)		
Determination of Hg	DIN EN 1483 (E 12)		
Content of lignocelluloses	Wet chemical methods of Savard, Kürschner and Hoffer		

## 2.3.2 Results of the characterization

### Thermo diagram

To get a first idea of the thermal behavior of the feedstocks, thermo-gravimetric determinations with a thermo-balance (Netzsch, STA 409) were carried out. The corresponding mass-loss curves as a function of time and temperature can be seen in the thermo-diagram Figure 2-5. The diagram is subdivided into two main sections. In the first section, there is an atmosphere of nitrogen whereas in the second one, the atmosphere is air. Under nitrogen atmosphere, the loss of moisture and volatiles can be shown. The moisture represents the physically bound water only. The water released by chemical reactions during pyrolysis is summarized within the volatiles. The constant residual mass at 700°C in the nitrogen atmosphere represents char including ash. The yield of the products obtained with the thermo-balance is representative for a slow pyrolysis. A fast pyrolysis might yield more volatiles. The second section of the diagram displays the combustion of the char under air atmosphere. The inorganic residual from the combustion is the ash.

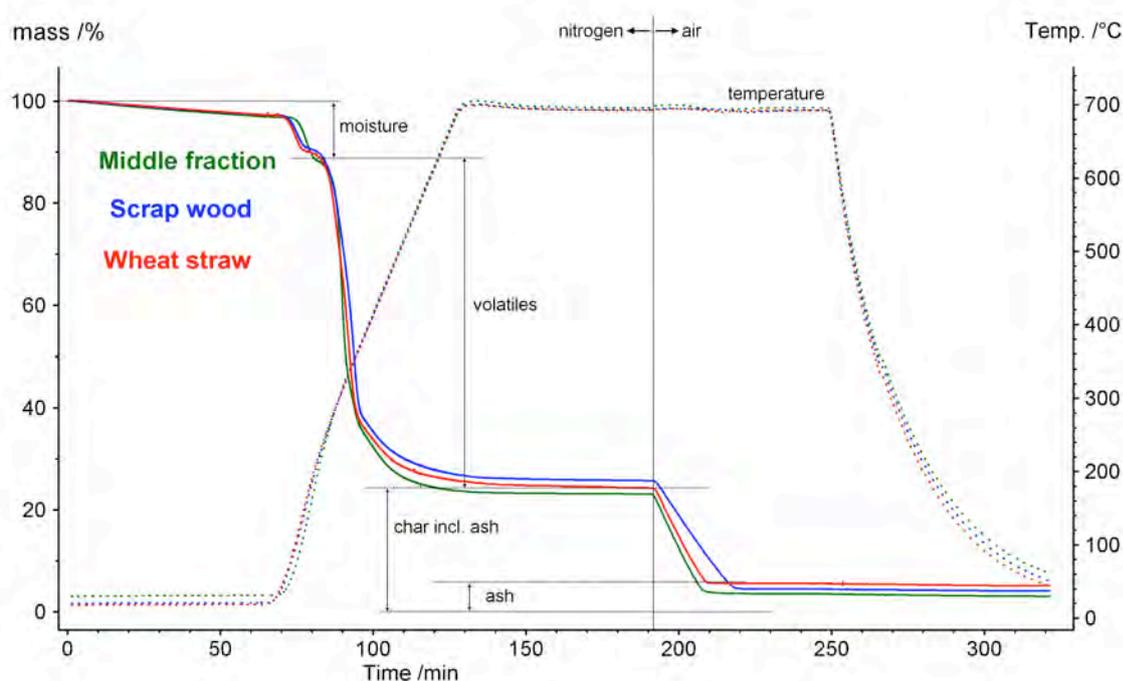


Figure 2-5: Results from the thermo-gravimetric determination: Slow pyrolysis of the feedstocks in a thermo balance; middle fraction: residues from flour production; Sample mass 200 mg, heating rate 10 K/min, pyrolysis in nitrogen, combustion in air (both 70 ml/min).

From Figure 2-4, it can be seen that the feedstocks investigated have a similar thermal behavior. Miscanthus has not been tested yet. The mass loss due to the release of moisture was in the range of approximately 10 %. The residue of the slow pyrolysis accounted to about 22-26 % of the initial feedstock mass. After combustion of the solid pyrolysis residues, the remaining ash was in the range of about 3-6 % of the initial feedstock mass.

### Proximate and ultimate analysis

The results for the proximate and ultimate analysis are shown in Table 2-2. The water and ash content measurements at KIT were performed with a macro-thermo-balance (LECO, TGA 701) following a special temperature program with stops at 550 °C and at 815 °C for the determination of the ash. The comparison of the ash contents for the two temperatures showed a slight effect of the ashing temperature. The ash contents were in all cases lower (0.1 to

0.5 mass-%) when applying a higher temperature. This is due to effects already mentioned before (see section 1.4). Water content ranged from about 3-17 % and ash content from about 1-7 %. From Table 2-2, it can be seen that, on dry basis, within a certain range, all feedstocks have a similar elemental composition and gross calorific value *HHV* (about 17-20 MJ/kg). The comparison of the values for wheat straw with those from literature (see Table 1-2 and Table 1-3) shows a good conformity for the elemental composition, ash content and gross calorific value. Scrap wood can be compared best to beech wood, whereby scrap wood has higher ash content and higher nitrogen, sulphur and chlorine values. This is probably due to the way the wood was processed.

From the external laboratory, values for the volatile content are given to be between about 75-80 mass-%. The contents of sulphur and chlorine both show the highest values for wheat straw. It has not been shown that this causes corrosion problems in the test facilities of the KIT.

Table 2-2: Results of the proximate and ultimate analyses performed KIT-internally and in an external laboratory; wf: water free.

		<b>Proximate and ultimate analysis</b>			
		results on dry basis			
		<b>Scrap wood</b>	<b>Middle fraction</b>	<b>Wheat straw</b>	<b>Miscanthus</b>
Water content	mass-%	10.5	9.4	2.8	17.3
Ash <sub>wf</sub> at 550°C	mass-%	3.9	2.6	6.8	-
Ash <sub>wf</sub> at 815°C	mass-%	3.4	2.5	6.3	1.7
volatiles *	mass-%	79.4	80.9	75.4	-
C	mass-%	47.9	44.7	45.6	48.7
H	mass-%	5.7	6.3	5.5	5.5
O at 550 °C	mass-%	39.9	44.5	41.2	-
O at 815 °C	mass-%	40.4	44.6	41.8	44.1
N	mass-%	2.7	1.8	0.6	<0.5
S *	mass-%	0.07	0.11	0.16	-
Cl total *	mg/kg	850	365	1560	-
HHV <sub>wetbasis</sub>	kJ/kg	17268	16166	17386	15333
HHV <sub>drybasis</sub>	kJ/kg	19251	18510	17868	18540

\*: measured externally

### Lignocelluloses composition

The compounds of lignocelluloses were determined in an external laboratory by the wet chemical methods of Savard and Kürschner and Hoffer. Table 2-3 shows the contents of cellulose, hemicelluloses and lignin for all three feedstocks.

Table 2-3: Results of the determination of composition of lignocelluloses.

		<b>Lignocelluloses</b>			
		<b>Externally measured</b>			
		<b>Scrap wood</b>	<b>Middle fraction</b>	<b>Wheat straw</b>	<b>Miscanthus</b>
Cellulose	mass-%	42.0	17.0	45.0	50.7
Hemicelluloses	mass-%	13.0	40.0	16.0	23.1
Lignin	mass-%	26.0	8.0	24.0	28.7

There are considerable differences in the lignocelluloses compositions. The residues of flour production (middle fraction) have a significantly higher content of hemicelluloses and much lower content of cellulose and lignin than the scrap wood, wheat straw and miscanthus. Those three feedstocks show a quite similar composition. It will be interesting to see how the lignocelluloses composition affects the product yields in the fast pyrolysis.

### **Ash composition**

The elemental composition of ash is of interest, because some elements have a catalytic effect on the reactions occurring during pyrolysis and therefore on the yields of gases, pyrolysis oil and char [12], [13]. It is expected that the heavy metals of the feedstocks are almost completely accumulated in the char as stated by [14], [15].

Trace elements of the feedstock ashes were measured in an external laboratory using melting and micro-wave disintegration methods. Miscanthus has not been measured yet. The results are represented in Table 2-4. The ash resulting from scrap wood showed clearly higher values for various elements, especially for the heavy metals. For instance, the content of Pb is by approximation a factor 300 higher in the scrap wood than in the middle fraction of flour production and wheat straw.

Table 2-4: Results of the feedstock ash analysis.

<b>Biomass ash composition at 550 °C</b>				
<b>Externally measured</b>				
results on dry basis				
<b>Ash analysis at ash 550 °C (melting desintegration)</b>				
		<b>Scrap wood</b>	<b>Middle fraction</b>	<b>Wheat straw</b>
Al	mass-%	1.9	0.5	0.3
Ba	mass-%	1.2	<0.1	<0.1
Ca	mass-%	10.6	2.3	6.4
Fe	mass-%	1.4	0.5	0.2
K	mass-%	2.3	11.5	13.7
Mg	mass-%	1.9	2.6	1.5
Mn	mass-%	0.4	<0.1	<0.1
Na	mass-%	2.9	0.2	0.2
P	mass-%	0.6	8.0	1.6
Si	mass-%	16.4	22.2	25.6
Ti	mass-%	3.5	0.2	0.3
<b>Ash analysis at ash 550 °C (micro-wave desintegration)</b>				
As	mg/kg	63	1.1	2.1
B	mg/kg	700	70	89
Cd	mg/kg	20	1	2.2
Co	mg/kg	30	2	2
Cr	mg/kg	370	40	30
Cu	mg/kg	650	100	57
Hg	mg/kg	<0.07	<0.05	<0.05
Mo	mg/kg	10	11	11
Ni	mg/kg	250	30	22
Pb	mg/kg	3000	10	13
Sb	mg/kg	56	<1	<1
Se	mg/kg	1	1	2
Sn	mg/kg	52	<3	<3
Sr	mg/kg	600	130	310
Te	mg/kg	3	2	2
V	mg/kg	31	3	7
Zn	mg/kg	6400	650	310

## 3 Feedstock selection suitable for HTC

### 3.1 Requirements for HTC feedstock

Due to the broad variety of feedstocks suitable for the HTC process, different kinds of pre-treatment processes are used in order to feed the HTC plant. Best case scenario is a wet feedstock which can be pumped into the reactor. If biomass like straw is used, it has to be cut into shorter pieces. A special pre-treatment has to be used for organic municipal waste, due to the high amount of inorganic waste which comes with it. For project purposes this is done manually, but for an industrial plant converting 60 – 70000 tons of organic waste per year, automatized pre-treatment processes have to be investigated.

Although Friedrich Bergius (German chemist) discovered the hydrothermal carbonization process in 1913 [16] the hydrothermal carbonization remains a new technology. The advantage of HTC is that this process can convert wet and dry industrial by-products, with low energy values to a higher energy product, the biocoal. The  $HVV_{dry}$  of the biocoal depends on the chemical composition of the feedstock.

### 3.2 Selection of the HTC Feedstocks

For BioBoost three different biomasses have been characterized:

- **Bio Energie Tonne** (BET - Organic municipal waste)
- **Spent grains from breweries**
- **Straw**

These feedstocks have several advantages:

- They are available in large quantities
- They are available at no cost, or even generate revenue like municipal organic waste, because there is no established conversion path yet

#### 3.2.1 Organic Municipal Waste

Organic municipal waste is a widely available feedstock in urban areas. It was delivered from a partner as it is collected. In Germany, the concept of the “Bio Energie Tonne” mixes organic (food rests etc.) and non-organic waste (metals, sand, silt, plastics etc.). Therefore, pre-treatment is required to separate organic waste from the rest. For the purposes of this study, this has been done manually.



*Figure 3-1: Organic Municipal Waste.*

### **3.2.2 Spent grains from breweries**

Spent grains from breweries is a feedstock very well suitable for the HTC process. It is wet and still contains enough dry matter for excellent carbonization results. However, this might differ between several breweries, therefore analysis is necessary prior to carbonization. The feedstock usually comes without contamination and it can be pumped easily.



*Figure 3-2: Spent Grains from Breweries.*

### **3.2.3 Straw**

Straw was used for comparison reasons of this feedstock. Straw is the synonym for dryness, and therefore it is not an ideal matter for the HTC process. Cut into smaller pieces it can be fed easily into the plant and it works very well, especially if it is mixed for example with spent grains from breweries, if dry matter content is too low.



Figure 3-3: Straw.

### 3.3 Physical and chemical characterization

In order to prove the properties and suitability of the biomass it is important to understand their physical and chemical behavior as feedstock for the different processes. For HTC it is essential to determine: the dry matter content, elemental composition (C, H, O, N, S), ash content, calorific value, etc.

#### Dry matter content

The definition of the dry matter content is explained on chapter 1.3

#### Elemental composition

The elemental composition gives an overview of a sample's content of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S). For HTC the carbon content is important. With this value it is possible to estimate the carbon concentration in the biocoal. All values are based on dry matter content percentage. It is also possible to calculate the value ash free. Table 3-1 shows the values of the three biomasses selected.

Table 3-1: Elemental composition.

		<b>BET<sup>1</sup></b>	<b>Spent grains</b>	<b>Straw</b>
Carbon	%DMC	22.2	48.7	47.9
Hydrogen	%DMC	3.4	6.9	6.13
Oxygen	%DMC	18.6	34.1	42.98
Nitrogen	%DMC	1.1	4.3	0.9
Sulphur	%DMC	0.39	0.39	0.09

<sup>1</sup>Municipal organic waste

## Calorific value

The explanation of the calorific value can be found in chapter 1.5. The following table shows the calorific values for the chosen feedstock.

Table 3-2: HHV for the mentioned feedstocks.

	BET <sup>2</sup>	Spent grains	Straw
HHV KJ/Kg DM	9.500	19.200	18.078

## Ash content

The ash content is the residual of combustion. Higher ash content by combustion will produce more slugging, because at higher temperatures the ash will melt and stick to the walls, depending on the ash melting point. This decreases the lifetime of the burner, therefore high ash content is not desired [18]. The following Table shows the ash content of the selected biomasses analyzed at 550°C.

Table 3-3: Ash content for the mentioned biomasses.

	BET <sup>2</sup>	Spent grains	Straw
Ash in % DMC	54	5.6	2

Also important is the content of the inorganic trace elements in the ash, especially K<sub>2</sub>O and Na<sub>2</sub>O. These two compounds have a great impact on the slugging potential. In the next Table the ash composition is shown. All measurements were analyzed by an external laboratory.

Table 3-4: Composition of ash for the mentioned feedstocks.

Ash composition at 550°C	BET	Spent grains	Straw
Cl (total) % DMC	0.36	0.001	n/a
P (total)% DMC	0.3	0.64	0.43
K <sub>2</sub> O% DMC	1.5	0.046	0.93
Pb% DMC	0.0041	0.0003	<0.02
Cd% DMC	0.00003	0.00003	<0.004
Cr (total)% DMC	0.002	0.0005	n/a
Cu% DMC	0.0041	0.0017	<0.004
Ni% DMC	0.0014	0.0011	<0.008
Hg% DMC	0.00009	0.00001	n/a
Zn% DMC	0.014	0.021	0.036
Ca% DMC	7.1	0.43	0.043
Fe% DMC	0.64	0.057	0.011
Mg% DMC	0.52	0.25	0.93
Mn% DMC	0.091	0.0074	n/a
Na <sub>2</sub> O% DMC	0.74	0.032	0.024
S% DMC	0.39	0.39	0.2
Sn% DMC	<0.0003	<0.0003	n/a
P <sub>2</sub> O <sub>5</sub> % DMC	0.79	1.4	0.98

<sup>2</sup>Municipal organic waste

## 4 Feedstock selection suitable for Catalytic Pyrolysis (CP)

For the catalytic pyrolysis performed at CPERI/CERTH a woody biomass, an energy crop and an agricultural residue will be evaluated as potential feeds for this technology.

### 4.1 Requirements for catalytic pyrolysis feedstock

Feedstocks for catalytic fast pyrolysis process should have in general similar characteristics with the feedstock used in the fast pyrolysis technology. The main difference concerns the ash content. In catalytic pyrolysis the ash content should be as low as possible in order to avoid catalyst poisoning and deactivation due to the ash metals. Regarding water content the catalytic pyrolysis feed should have less than 10 mass-% in order to ensure a high energy efficiency of the process and high product quality, taking into account that water yield from catalytic pyrolysis is higher compared to thermal pyrolysis.

*Pre-treatment:* The pre-treatment (drying, separation of impurities and grinding) of the feedstock prior to the catalytic pyrolysis process should be similar to that described in section 2.1 for the fast pyrolysis. Thus, it is necessary to dry the feedstock in order to reduce its water content, then the removal of impurities should take place and finally the grinding of the feedstock is necessary. For the pilot plant operation in CPERI a size around 250-1000 microns is necessary, however, for a commercial plant a size of about 5 mm is crucial for having a homogenous feed into the reactor and to realize a sufficient heat transfer from the heat carrier to the biomass particles.

### 4.2 Selection of the CP Feedstocks

For BioBoost four different biomasses have been characterized and evaluated as potential feeds for CP tests:

- Woody biomass: Lignocel
- Agricultural residues: Wheat straw
- Energy crop: Miscanthus or Cardoon

For the agricultural residue the wheat straw was selected as reference since it will be used in all three technologies for comparison purposes. This wheat straw will be supplied by KIT to CERTH. For the woody biomass a commercially available beechwood feed (Lignocel) will be used since it is available in large quantities and it is used as reference in CPERI/CERTH in the last years. For the energy crop we examined two options, the Cardoon and the Miscanthus. The Cardoon is a popular plant in the Mediterranean area, with minimum cultivation requirements. Currently large amounts of cardoon can be found in uncultivated areas and as road-side vegetation. This biomass is received either as dried plant parts or in pelletized form. Miscanthus is a widely accepted energy crop, very well adapted in the European climate and is currently cultivated at many parts of Europe. It is received either as dried straw or in the form of pellets.



Figure 4-1: Cardoon Plant.



Figure 4-2: Miscanthus plant.



Figure 4-3: Lignocel.

### 4.3 Feedstock characterization

The selected biomasses were characterized as far as their physicochemical properties are concerned and the results are presented in Table 4-1.

Table 4-1: Analysis of biomasses selected for CP.

<b>Proximate and ultimate analysis (results on dry basis)</b>				
	<b>Lignocel</b>	<b>Wheat straw</b>	<b>Cardoon</b>	<b>Miscanthus</b>
Water content (mass-%)	7.6	8.7	13.3	6.9
Ash <sub>wf</sub> 650°C (mass-%)	0.7	4.5	15.4	2.5
C (mass-%)	45.9	44.1	38.1	45.6
H (mass-%)	6.4	6.2	5.3	6.0
O (by difference) (mass-%)	46.9	45.2	41.2	45.9
HHV <sub>drybasis</sub> , MJ/kg	19.09	18.24	15.85	19.2
<b>ICP analysis of biomass ash (ppm)</b>				
K	130	4766	-	5720
Na	452	340	-	654
Mg	365	855	-	-
Fe	120	202	-	-
Al	-	305	-	-
Ni	-	4	-	-
V	-	0.55	-	-
Ca	1620	1955	-	-

The hemicellulose, cellulose and lignin content of the biomasses are presented in Table 4-2. The lignin content was determined according to the official method TAPPI222, the holocellulose content after small modifications of the Wise method and hemicellulose by difference from holocellulose after employing TAPPI 203.

Table 4-2: Lignocellulosic content of biomasses selected for CP.

<b>Lignocelluloses</b>				
	<b>Lignocel</b>	<b>Wheat straw</b>	<b>Cardoon</b>	<b>Miscanthus</b>
Cellulose, mass-%	39.3	44.9	34.0	36.7
Hemicelluloses, mass-%	37.1	23.7	28.2	27.3
Lignin ( <i>acid insoluble</i> ), mass-%	21.8	20.6	18.2	23.3
Lignin ( <i>acid-soluble</i> ), mass-%	n.a.	4.4	16.8	4.9

Among the selected biomasses, wheat straw appears to have the highest cellulose content, while cardoon seems to be the richest in total lignin. The ash content of the biomasses should be taken into consideration, as it is known to affect the pyrolysis outcome, in which case the high ash content of cardoon might have a high impact on the produced bio-oil. Some pre-treatment methods, e.g. washing with water, could be employed prior to pyrolysis. Based on ash data it seems that the Miscanthus is a more preferable feed to CP compared to Cardoon. The selected biomasses were also subjected to TGA analyses in order to review their decomposition profile, and results are presented in Figure 4-4.

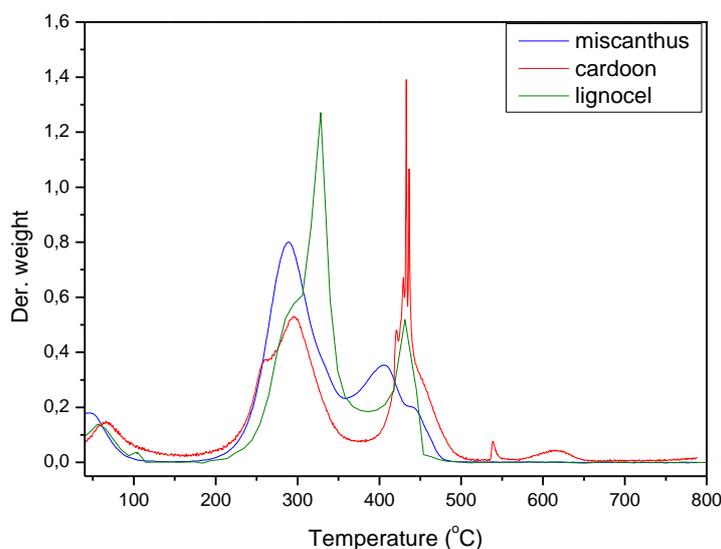


Figure 4-4: TGA graph of biomasses (derivative weight vs temperature).

Thermogravimetric analysis was performed under air in order to view the decomposition profile of biomass's main constituents. The peaks from 250 to 350°C are attributed to hemicellulose and cellulose, while the peaks above 400°C are attributed to lignin.

The general conclusion from the above characterization work is that the most promising feed for CP technology is a woody feedstock and thus Lignocel will be mainly used in BioBoost project. This feed has low ash content with low K, Mg and Ca and thus, it is expected to have only a small effect on catalyst deactivation. Moreover, its moisture content and the lignin content are relatively low. The second feed will be the Miscanthus feed that – as discussed above – is better compared to cardoon. It has lower lignin content and the most important lower ash. Finally the straw will be used for comparison purposes with the other technologies.

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