



**SES6-CT-2003-502705**

**RENEW**

**Renewable fuels for advanced powertrains**

**Integrated Project**

**Sustainable energy systems**

# Definition of a standard biomass

**Deliverable WP2.1 /D 2.1.1**

Due date of deliverable: 12-2004

Actual transmission date: 01.12.2004

Start date of project: 01-01-04

Duration: 48 months



Forschungszentrum Karlsruhe  
In der Helmholtz-Gemeinschaft

*Forschungszentrum Karlsruhe GmbH  
Weberstr.5  
76133 Karlsruhe  
Germany*

Revision 1-12

<b>Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)</b>		
<b>Dissemination Level</b>		
<b>PU</b>	Public	<b>PU</b>
<b>PP</b>	Restricted to other programme participants (including Commission Services)	
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission Services)	
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	



Report prepared under the framework of project:  
RENEW – Renewable fuels for advanced power trains  
Contract nr.: FP6 SES6-CT-2003-502705  
Subproject 5 WP2.1 Feedstock definition

# Definition of a standard biomass

Authors:

FZK  
CUTEC  
BKG

R.Stahl, E. Henrich,  
H.J. Gehrman, S. Vodegel,  
M. Koch



# Contents

<b>1 Introduction</b>	<b>3</b>
<b>2 Bulk physical/chemical characterisation of biomass</b>	<b>3</b>
<b>2.1 Moisture content</b>	<b>3</b>
<b>2.2 Proximate Analysis</b>	<b>4</b>
<b>2.3 Ultimate Analysis</b>	<b>6</b>
<b>2.4 Heating value</b>	<b>7</b>
<b>2.5 Ash</b>	<b>8</b>
Ash content	8
Ash composition	8
Ash melting behaviour	9
<b>3 Biomass used at the demonstration plant at Güssing</b>	<b>10</b>
<b>Outlook</b>	<b>10</b>
<b>Appendix</b>	<b>11</b>
<b>References</b>	<b>12</b>

## 1 Introduction

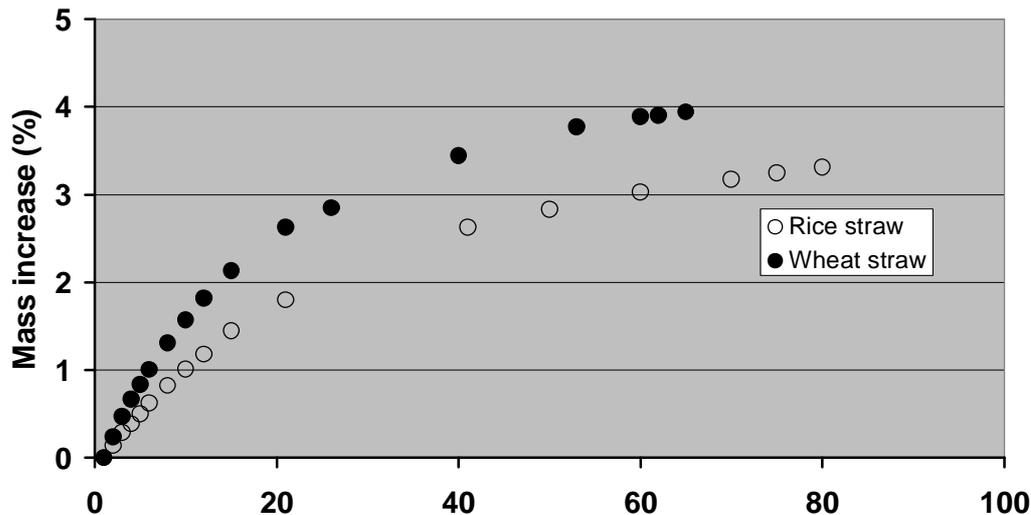
The investigations in subprogram 2 (SP 2) focus on the optimisation of the complete process chain for the production of FT fuel from a widely varying nature of solid biomass feedstocks. The characteristics of the individual biomass varies: Wood is a relatively clean fuel and traditional technologies for wood combustion are well developed. Herbaceous by-products from agriculture, mainly cereal straw and straw like residues, are among the cheapest products from agriculture. Contrary to wood these residues inevitably contain more ash and heteroatoms, especially much potassium and chloride. As a consequence they need more expensive fertiliser. The inorganic elements are constituents of bio-catalytic systems, which are needed for the faster metabolism. Slowly growing wood usually contains <1% ash (without bark). Faster growing biomass like straw or hay contains 5 to 10% ash, and typical K- and Cl- contents are in the 1% range. Technologies for the use of herbaceous biomass residues are more complex and not well developed. The large arisings of agricultural by-products for energy production correspond to ~5 – 10 % of the world primary energy consumption. This is a significant fraction and justifies the development of a special gasifier technology. SP2 investigates the gasification of biomass via autothermal fluidised bed gasification at CUTEC and via the pressurised entrained flow gasification in a GSP-type gasifier compatible with much ash at FZK (BTL2 process) /1,2/. To compare the results, both routes are tested on pilot scale gasifiers with identical biomass materials. Several agricultural products have been identified and characterised. Among these two standard biomasses have been selected to be used in both gasification technologies for comparative reasons.

## 2 Bulk physical / chemical characterisation of biomass

Already available information of the properties of biomass materials is useful in order to evaluate their suitability as chemical feedstock in different processes. This report summarises information on a variety of such properties. In evaluating gasification feedstocks, the following properties are generally useful: water content, proximate (thermo-chemical behaviour) and ultimate (elemental composition) analysis, heats of combustion and ash analyses (see appendix table A1). These provide information on volatility of the feedstock, elemental analysis and heat content. The elemental analysis is particularly important in evaluating the feedstock in terms heating value and of potential technical problems like reactor slagging and potential pollution problems.

### 2.1 Moisture or water content of fuels

The moisture content of a solid is expressed as the quantity of water per unit mass of the dry solid. In this work the wet basis water content is used which is the ratio of the total mass of moisture in the original sample to the original wet mass of sample. Water can be determined by different methods. The conventional determination of moisture is drying in an oven in air to constant weight at 105°C. Prolonged drying in the oven can result in loss of volatile constituents due to decomposition, distillation or oxidation of the biomass. Typical initial values extend from ~50% to 10%. The moisture content can change during handling. Wheat straw has got about 15 – 10% moisture as delivered. During storage in the laboratory it decreases down to an equilibrium value of about 8%. Very dry biomass materials are hygroscopic. For most analytical procedures, biomass was milled in a cryo mill (mean particle size ~ 0,12 mm) and completely dried. As figure1 shows these materials show a very rapid

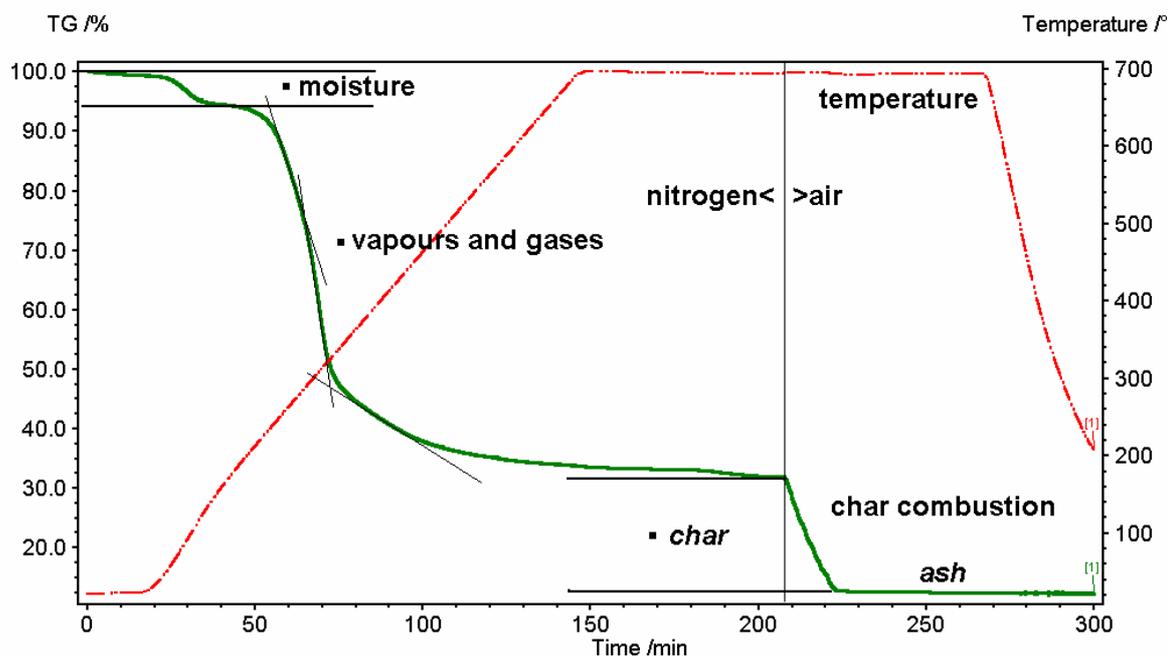


**Figure 1:** Moisture uptake of dried (105°C, 24 h) biomass with a mean particle size of 0,12 mm

uptake of moisture. As a consequence the dried material have to be stored carefully in closed vessels. Even short time handling has to be performed in a completely dry atmosphere. Correct handling is precondition for reliable analytical results.

## 2.2 Proximate Analysis

The proximate analysis classifies the fuel in terms of its moisture (M), volatile matter (V), fixed carbon (FC) and ash. The thermal behaviour of biomass has been studied by measuring the rate of weight loss of the sample as a function of time and



**Figure 2:** Slow pyrolysis of wheat straw in a thermobalance  
 Sample 230 mg, heating rate 5 K/min, pyrolysis in nitrogen, combustion in air, both 70mL/min

temperature (thermo gravimetric analysis TGA). The observed rates are not only functions of time and temperature, but also of the size and the density of the sample. TGA offers an understanding of the process under well-controlled laboratory conditions. The dynamic TGA measurements yield data equivalent to a standardised proximate analysis. In the test procedure the biomass samples (200mg straw or straw like materials) were heated up to 700°C in a thermobalance with different heating rates (0,5 – 50K/min) in a nitrogen atmosphere (70mL/min).

Figure 2 shows a typical thermodiagramm of straw, subdivided into two main sections. The first part in nitrogen atmosphere shows the loss of moisture and volatiles. The moisture determined represents physically bound water only; water released by chemical reactions during pyrolysis is summarised among the volatiles. The pyrolysis yield is representative of that for slow pyrolysis processes; fast pyrolysis techniques employing very rapid heating rates might yield more volatile matter. The second part is performed in air. The ash content is determined by combustion of the fixed carbon. The resulting ash fraction is not representative of the original ash due to the oxidation process employed in its determination. Thus

$$\text{moisture} + \text{vapours} + \text{fixed carbon} + \text{ash} = 100 \text{ m\%}.$$

**Table 1:** Proximate analysis data of selected biomass materials (dry) (m%)  
Values in brackets are from literature /3,4,5/

dry	Wheat		Rice		Hay	Cotton stalks	Wood
	straw	bran	straw	husks			
Volatiles	69 (71,3)	70	59 (69)	66 (64)	65	72	84 (83)
Fixed Carbon	23 (19,8)	22	19 (17)	17 (16)	21	24	16 (17)
Ash	8 (8,9)	8	21 (13)	18 (21)	14	4	0,3 (0,5)

**Table 2:** Proximate analysis data of selected biomass materials (m%, dry and ash free)

daf	Wheat		Rice		Hay	Cotton stalks	Wood
	straw	bran	straw	husks			
Volatiles	75	76	75	79	76	75	84
Fixed Carbon	26	24	24	21	24	25	16

Table 2 shows the results of the proximate analysis calculated on a dry and ash free (daf) basis. All the studied fast growing biomass materials show almost identical values for volatiles (~76 %) and fixed carbon (~24%). For the woody biomass the amount of volatiles/char is about 8 % higher/lower. The volatiles consist of permanent gases like CH<sub>4</sub>, CO<sub>2</sub> and CO and vapours, which form the bio-oil after condensation. The amount of gases and bio-oil is expected to be about 18+6% and

60 +/-15% respectively, depending on the special pyrolysis conditions. More detailed studies will be done in SP2 working package 2.2 I - task 2.2.2 "Pyrolysis of biomass".

### 2.3 Ultimate Analysis

The ultimate analysis generally reports the elemental carbon (C), hydrogen (H), nitrogen (N), sulphur (S) composition and oxygen (O) very often by difference in the solid fuel. In order to avoid confusion and to give a good representation of the fuel itself, an ultimate analysis is performed and reported on a dry basis, because otherwise moisture is indicated as additional hydrogen and oxygen. For fast growing biomass materials like straw, the determination of chlorine is important, because it represents a possible pollutant and corrosive agent in pyrolysis, gasification and combustion systems. A number of instruments have been developed to determine the elemental C, H, N, S and O composition. In some cases C, H, N and S can be determined simultaneously. In this work oxygen also has been determined by direct

**Table 3:** Ultimate analysis data of selected dry biomass materials (m%, dry)

	Wheat		Rice		Hay	Cotton stalks	Wood
	straw	bran	straw	husks			
<b>C</b>	45,7 (43,2)	47,7	39,2 (41,8)	44,5 (41)	45,9	46,6 (39,5)	48,6 (50)
<b>H</b>	5,7 (5,0)	6,4	4,8 (4,6)	6,3 (4,3)	6,0	5,6 (5,1)	6,1 (6)
<b>O</b>	43,3 (39,4)	42,0	36,4 (36,5)	36,9 (36)	39,4	42,8 (39,1)	45,0 (43)
<b>N</b>	0,5 (0,6)	2,8	0,4 (0,7)	0,9 (0,4)	2,3	0,7 (0,4)	0,2
<b>S</b>	0,3 (0,1)	0,3	0,2 (0,1)	0,6 (0,01)	0,3		
<b>Cl</b>	0,7 (0,3)		1,9 (0,3)	(0,1)	1,0	0,5 (0,1)	< 0,1

**Table 4:** Ultimate analysis data of selected biomass materials (m%, dry and ash free)

	Wheat		Rice		Hay	Cotton stalks	Wood	Mean
	straw	bran	straw	husks				
<b>C</b>	47,8	48,1	48,4	49,9	49,0	48,7	48,6	48,6 +/-0,7
<b>H</b>	6,0	6,4	5,9	7,0	6,3	5,9	6,1	6,3 +/-0,4
<b>O</b>	45,3	42,3	44,9	41,3	41,9	44,7	45,1	44 +/-2
<b>N</b>	0,5	2,8	0,5	1,0	2,4	0,8	0,2	
<b>S</b>	0,3	0,3	0,3	0,7	0,3	0,0	0,0	

measurement – not by difference - after modification of the instrument. Most of the systems employ catalytic combustion with pure oxygen to decompose the sample to nitrogen, water, carbon dioxide and sulphur dioxide, which are then determined quantitatively by chromatography using flame ionisation or thermal conductivity detectors. Oxygen is determined by catalytic conversion to carbon monoxide. For the analysis of fast growing biomass samples an instrument (Vario EL) from Elementar GmbH, Hanau, Germany has been used. Chlorine is determined separately after combustion to HCl in a separate analyser. The results are summarised in tab. 3.

Calculated on a dry and ash free basis the typical composition of woody and herbaceous biomass materials is very similar (tab.4). The organics CHO-composition of lignocellulose like wood or straw is not much different and approximately represented by  $C_6H_9O_4$ . For quick estimates a more simplified formula is useful:  $C_3(H_2O)_2$ . It may be viewed at as a mixture of 50wt% carbon with 50 wt% water.

## 2.4 Heating value

The heating value may be reported on two bases. The higher heating value (HHV, cross heating value)) represents the heat of combustion relative to liquid water as the product. The lower heating value (LHV) is based on gaseous water. The difference in the heating value is the latent heat of the product water. For many kinds of coal the gross heating value ranges from 20 to 30 MJ/kg /6/. However, nearly all kinds of lignocellulosic biomass feedstocks fall in the range 15-19MJ/kg. The values for most woody materials are 17-19 MJ/kg; for most agricultural residues, the heating values are about 15 – 17 MJ/kg. All heats reported here are HHV on a dry basis. The heating value of carbon feed stocks is determined employing an adiabatic bomb calorimeter that measures the enthalpy change between reactants and products at 25°C. A common method for estimating heating values of solids is the Dulong-Bertholot equation which permits estimation from the ultimate analysis. Table 5

**Table 5:** Higher heating values (HHV) of selected biomass materials (dry)

HHV (kJ/kg)	Wheat		Rice		Hay	Cotton	Wood
	straw	bran	straw	husks		stalks	
<b>Experimental</b>	<b>17100</b>				<b>17100</b>		
<b>Calculated <sup>1)</sup></b>	<b>17200</b>	<b>19000</b>	<b>14700</b>	<b>18600</b>	<b>18200</b>	<b>17400</b>	<b>18400</b>
<b>Calculated <sup>2)</sup></b>	<b>19300</b>	<b>20300</b>	<b>15300</b>	<b>17600</b>	<b>18800</b>	<b>19300</b>	<b>20400</b>
<b>Literature <sup>3)</sup></b>	<b>17100</b>		<b>15400</b>	<b>15700</b>	<b>16500</b>	<b>15200</b>	<b>19000</b>

1)  $HHV = 339 C + 1214(H-O/8) + 226 H + 105 S$

2)  $HHV = 20490 - 271 \text{ Ash}$

3) <http://www.ecn.nl/phyllis/> <http://www.vt.tuwien.ac.at/biobib/>

presents the calculated and experimental HHV for selected biomass fuels. If biomass is considered as  $C_6H(H_2O)_3$  with different ash contents the HHV can be calculated according to Ebeling and Jenkins /7/ from the dry ash free heating value:

HHV (kJ/kg) =  $K - 271 A$  where K is the HHV of lignocellulose daf (20490 kJ/kg) and A is the percent ash by weight on a dry basis. As table 5 shows these calculated HHV agree within 10% error with the experimental and calculated (Dulong-Bertholot equation) results.

## 2.5 Ash

### 2.5.1 Ash content

The ash content of woody biomass without bark is in general below 1%. In contrast, fast growing biomass has an ash content up to 20% (e.g. in some types of rice straw). All fast growing herbaceous biomass like straw, hay or leafs etc. contain about an order of magnitude more ash and heteroatoms than wood. Typical ash contents of straw or hay are 5 to 10%. Higher ash and heteroatom concentrations are also an indication of higher fertiliser requirements for the faster growing species. Nature recovers the valuable inorganic constituents after fast growth e.g. from the older wood parts. In some cases soil impurities can considerably contribute to the ash content.

### 2.5.2 Ash composition

Contrary to clean fuel wood, combustion and especially gasification technologies for the poorer herbaceous bio-fuels are not well developed. The high potassium content lowers the ash sintering temperature sometimes to  $< 700^{\circ}\text{C}$ . At combustion or gasification temperatures required for a fast fuel conversion, the ash becomes sticky and increases the risk of reactor slagging. Most of the chlorine is released as HCl into the gas phase. Consequences are corrosion in heat exchangers

**Table 4:** Percentage ash composition of selected dry biomass materials  
values in brackets are from Literature (3,4,5)

	Wheat		Rice	Hay	Cotton	Wood
	straw	bran	straw		stalks	
$\text{K}_2\text{O}$	2,2	1,0	6,2	4,0	0,5	0,04
$\text{CaO}$	0,3	0,1	0,5	0,4	1,7	(0,13)
$\text{SiO}_2$	3,6	$<0,1$	9,9	0,6	0,4	(0,08)
$\text{Cl}$	0,7	$<0,1$	1,0	1,0	0,5	( $<0,001$ )
$\text{P}_2\text{O}_5$	0,2	0,5	$< 0,1$	0,7	$< 0,1$	0,02
$\text{Fe}_2\text{O}_3$	$< 0,1$	$< 0,1$	0,6	$< 0,1$	1,0	(0,004)
$\text{MgO}$	0,1	$<0,1$	0,2	$<0,1$	0,2	0,02

and hot gas ducts, poisoning of downstream catalysts or formation of toxic polychlorinated dioxins or furans at unsuitable combustion conditions. Alkali salts

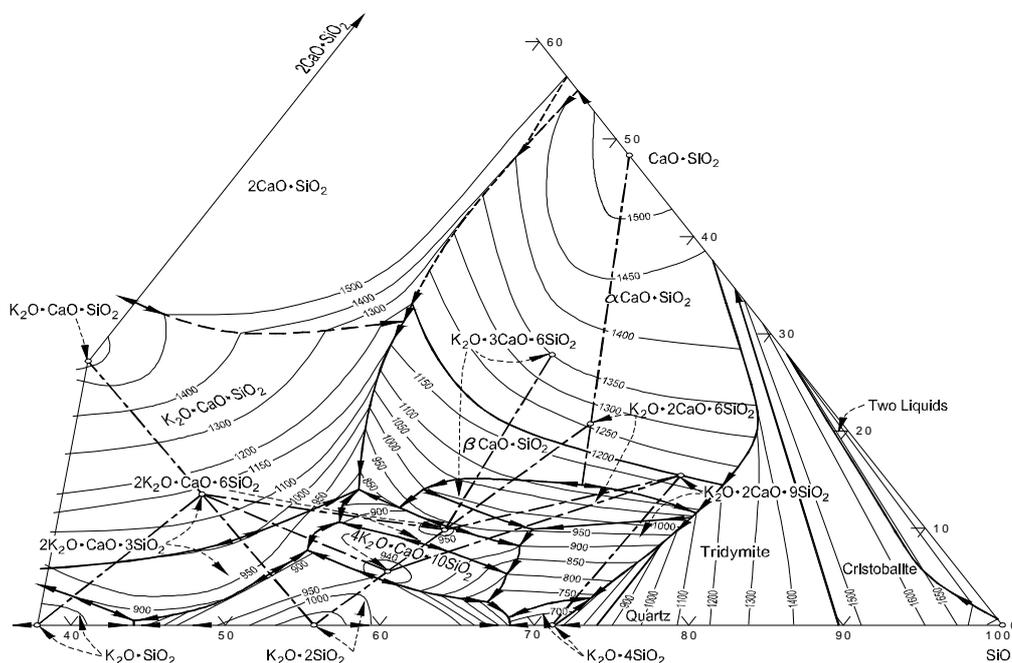
become volatile at temperatures  $> 650^{\circ}\text{C}$ ; deposition of alkali chlorides, hydroxides or low melting eutectics can cause serious corrosion and plugging of pipes. The main ash components are given in tab.4.

### 2.5.3 Ash melting behaviour

In the entrained flow gasifier as well as in a fluidised bed gasifier the ash melting behaviour is a very important factor for a suitable operating temperature in the gasifier. Between the CUTEC institute and FZK it has been considered to use the prepared wheat straw chops from FZK and the wood from CUTEC in both test facilities for comparison reasons. From the phase diagram /8/ of the system  $\text{SiO}_2 \cdot \text{K}_2\text{O} \cdot \text{CaO}$  the melting temperature of the wheat straw ash was estimated to be about  $1050 - 1200^{\circ}\text{C}$ . Experimental results under reducing atmosphere are given in table 5.

**Table 5:** Thermal behaviour of selected ashes

	Wheat straw	Wood
<b>Estimated Flow</b>	<b>1100,0</b>	
<b>Experimental Densification</b>	<b>770,0</b>	<b>1140,00</b>
<b>Distortion</b>	<b>830,0</b>	<b>1240,00</b>
<b>Hemispherical Flow</b>	<b>1100,0</b>	
<b>Flow</b>	<b>1300,0</b>	



**Figure 3:** Phase diagram of the system  $\text{SiO}_2 \cdot \text{K}_2\text{O} \cdot \text{CaO}$  /8/

### 3. Biomass used at the demonstration plant in Güssing

The specifications of the biomass for the demonstration plant in Güssing are given in table 6. Due to the plant design it is only able to use wood chips with a size of 10 – 50 mm and a water content of about 25+-10%.

### 4. Outlook

We propose to simplify and unify the treatment of the most important ligno-cellulosic biomass in the following way: The CHO composition of the organic part of straw, wood....including several percent of extractives, proteins etc. is represented by the following formula for daf lingo-cellulose

**Table 6:** Biomass characteristics for the Güssing plant

		<b>Wood</b>
<b>Volatiles</b>	<b>wt% daf</b>	<b>82</b>
<b>Ash</b>	<b>wt% dry</b>	<b>0,5 - 1,0</b>
<b>C</b>	<b>wt% daf</b>	<b>48,40</b>
<b>H wt% daf</b>	<b>wt% daf</b>	<b>6,10</b>
<b>O wt% daf</b>	<b>wt% daf</b>	<b>45,30</b>
<b>N wt% daf</b>	<b>wt% daf</b>	<b>0,21</b>
<b>S wt% daf</b>	<b>wt% daf</b>	<b>0,01 -0,02</b>
<b>Cl wt% daf</b>	<b>wt% daf</b>	<b>0,003</b>
<b>LHV</b>	<b>MJ/kg daf</b>	<b>17,70</b>

- $C_6H_9O_4$ , HHV = 20,4 MJ/kg,
- Ash is added with zero heating value,
- Moisture is added with corresponding LHV-corrections.

The results of the feedstock definition have been discussed in the SP2 session during the RENEW meeting in Güssing. Two representative biomass

feedstocks have been selected by CUTEC (Wood) and FZK (wheat straw). These standard biomass materials will be used both during the experimental campaigns at the CUTEC institute and at FZK. It is planned to compare the results of the gasification experiments (raw gas composition, gasification efficiency, .....).

## Appendix

**Table A1:** Testing procedures for bulk physical / chemical characterisation of biomass

Water content	DIN 51718
Heating value	DIN 51900-1/2
Ash content	DIN 51719
Ash composition	DIN 51729-10
Proximate Analysis	DIN 51004/5/6/7
Ultimate analysis	C,N,H,S combustion in oxygen flow

Further analytical procedures are given by the American Society for Testing and Materials (ASTM) /9/. These procedures were initially developed for coal, but the same ASTM methods have been widely used for biomass engineering work.

- /1/ E. Henrich, E. Dinjus, D. Meier, F. Weirich; 12<sup>th</sup> EU Conf. on Biomass for Energy and Industry, Amsterdam, 17. - 22. June 2002, Proc. p. 628
- /2/ E. Henrich, F. Weirich; Pressurised Entrained Flow Gasifiers for Biomass, Environmental Engineering Science 21(1) 2004, 53-64
- /3/ Domalski, E.S., Milne, T.A. "Thermodynamic data for biomass materials and waste components" The American Society of Mechanical Engineers, NY 1985.
- /4/ Schmid, A., Zschetzsche, A., Hanttsch-Linhart, W., „Analyse von biogenen Brennstoffen“, TU Wien 1993
- /5/ Hartmann, H., Böhm, Th., Maier, L.; "Naturbelassene biogene Festbrennstoffe" Institut und Bayrische Landesanstalt für Landtechnik der TU München, München 2000.
- /6/ Winnacker, K., Steiner, R., Harnisch, H., „Chemische Technologie“, 5 Carl Hanser Verlag München Wien 1981
- /7/ Ebeling, J.M., Jenkins, B.M., "Physical and chemical properties of biomass fuel", American Society of Agricultural Engineers, Winter meeting December 13-16, 1983, Chicago, Illinois.
- /8/ Levin, E., Ernest, M., Robbins, C.R., McMurdie, H.F., "Phase Diagrams for Ceramists", American Ceramic Society, Ohio 1964.
- /9/ American Society for Testing and Materials; <http://www.astm.org>

