Low temperature pyrolysis of agricultural residues – first results of a pilot plant

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A. Introduction

Woody biomass is already short in many European countries due to the increasing use of biomass for different applications, especially for CHP. Therefore, the price for woody biomass went up steadily during the last years. Low grade biomass which is cheap and regional available in large amounts, such as agricultural or industrial residues (e.g. straw, sludges) can not be used in conventional plants due to their properties (e.g. high chlorine, nitrogen, sulphur, and/or potassium contents). A pyrolysis process can be used to split up the biomass in a volatile fraction poor in undesired substances (Cl, N, S, Na and K) and a char fraction where these substances are concentrated. In this way cheap biomass can be used for co-firing in existing fossil fuel power stations without the danger of corrosion, deposition, and emission problems. The aim of the project is the development and demonstration of a biomass pre-treatment process based on pyrolysis in the temperature range between 400-600 °C to split the energy in the biomass into volatiles with a low content of the above mentioned undesired compounds and char, where most of these pollutants are concentrated. The volatiles can be fed into a fossil fuel power station to replace a certain amount of fossil energy by a renewable energy without the danger of corrosion, deposition, emission problems or the problem to reduce the ash quality in case of a coal fired power station

B. Principle of Pyrolysis

Pyrolysis is a process to convert biomass directly into solid, liquid and gaseous products by thermal decomposition in absence of oxygen. Pyrolysis is a very complex process. Many different reactions take place and can be influenced by numerous factors. The influencing parameters are chemical or physical pretreatments of raw material, heating rate, reactor type, pyrolysis temperature, residence time, pyrolysis atmosphere and particle size [1]. Biomass pyrolysis can be divided into four different stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition. [2] Pyrolysis is always a step within combustion and gasification processes where it is followed by total or partial oxidation of the primary products. An advantage of the pyrolysis process is that pyrolysis products are easily storable and transportable. Pyrolysis of ligno-cellulosic biomass is a very complex process of interdependent reactions. Nevertheless, it can be reduced to a simple kinetic model. [3] The yield of main products: liquid, char and gas depends especially on the pyrolysis temperature. At high temperatures liquid products are obtained, lower temperatures favour high char yields. [4]

C. Description of the pilot plant

The externally heated rotary kiln pyrolysis reactor in Dürnrohr is an innovative process technology which can also be used for high capacities. The design fuel power is about 3 MW, the pyrolysis gas capacity is about 1.5 MW. Approximately 0.6 t/h straw can be processed in the rotary kiln. The combustible straw is characterized by a high ash fraction and its culm shape. The process is operated at low temperatures (450 to 630 °C) to prevent an entry of corrosive ash elements (K, Cl, S, etc.) and additional emissions in the steam boiler of the coal fired power plant. An energetic use of the pyrolysis-charcoal (approximately 40-50% of the original heating value) occurs separately in a fluidised bed reactor.

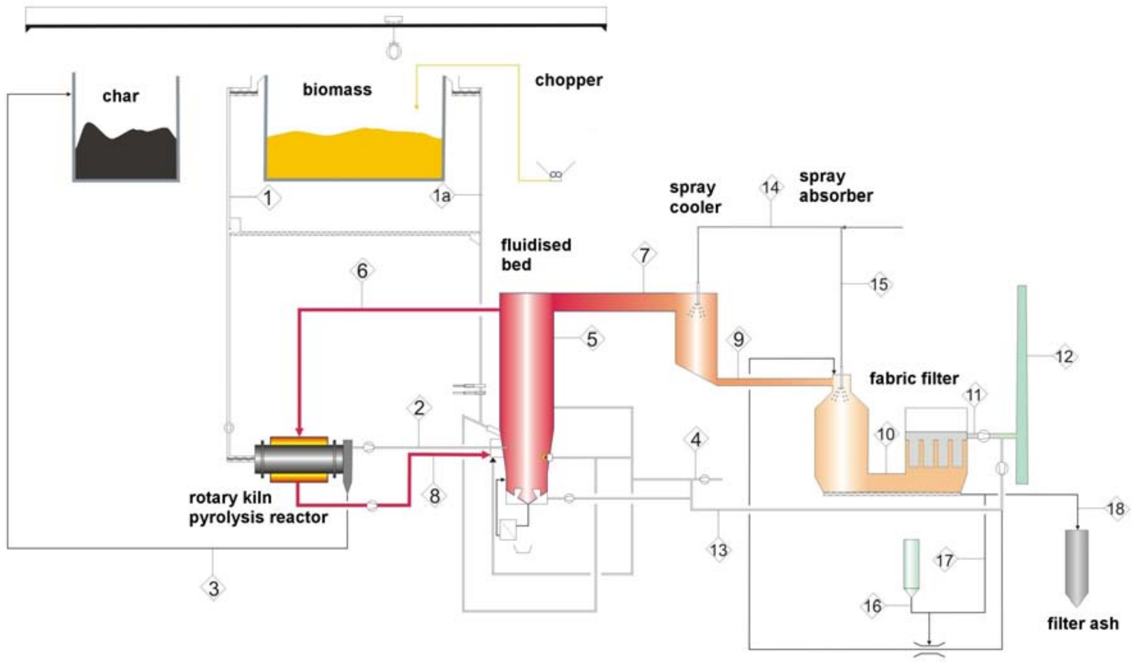

Figure 1: Flow sheet of the pilot plant

D. EXPERIMENTAL WORK

Several analytical methods are used to get more insight about the behaviour during pyrolysis. The main compounds of the pyrolysis gas are measured with a permanent gas measurement system. For the analytical determination of water and organic liquids in the pyrolysis gas phase two complementary methods are used: gravimetric determination and GC-MS determination. Fuel and char samples have been taken corresponding to the different measurements. First test runs were carried out at pyrolysis gas temperatures ranging from 560 to 630 °C.
Different agricultural residues have been under investigation.

- Straw
- Maize straw
- Oil Palm kernels
- Reed straw
- Sorghum straw
- Miscanthus straw
- Straw pellets

E. RESULTS AND DISCUSSION

Organic liquids can be classified due to the viscosity. Thereby liquids differ in low viscous pyrolysis oils and high viscous tar. The components are a mixture of alcohols, furans, aldehydes, esters, phenols, organic acids and oligomer carbohydrate and lignin products. The composition depends on the raw material and the pyrolysis process. The amount of gravimetric tar during the pyrolysis operation varies between 40-80 g/Nm^3. The actual high amounts of gravimetrical tars at pyrolysis gas temperatures between 560-630° C were expected. A decreasing amount of gravimetric tar at higher pyrolysis gas temperatures is observable. The lower content of gravimetric tars at higher pyrolysis gas temperatures is explained by the increasing emergence of small gaseous molecules from the cellulose-based tars (alcohols, aldehyds, ketons and carbon acids). The reactions to mention are dehydration, decarboxylation and decarbonylation. During pyrolysis operation the amount of the sum of GC/MS tars ranged between 27-42 g/Nm^3 with a slight decrease at higher temperature. The relative proportion of the substance groups is based on the sum of single compounds of GC/MS tars and displayed in Figure 2. The group of phenols is the main component with a relative proportion of 68-74 % of the GC/MS tar. The aromatic compounds (rel. proportion 8.2-13 %) and the naphthalenes (rel. proportion 8-13 %) as well as the PAH (without naphthalenes) (rel. proportion 5-9 %) and the furans (rel. proportion 2.7-3.5 %) are also frequently found. The aromatic compounds with nitrogen contribute only a small relative proportion (1.2-1.6 %). The main component is explained by the nature and formation of the tars. At the applied temperatures (600-630° C) for the pyrolysis process, mainly primary tars are found. The tars formed from lignin are mostly substituted phenols, which explain the high amount of phenols. The linage of phenols with the lignin tar formation is reasonable due to the aromatic likely phenol base structure of the lignin.

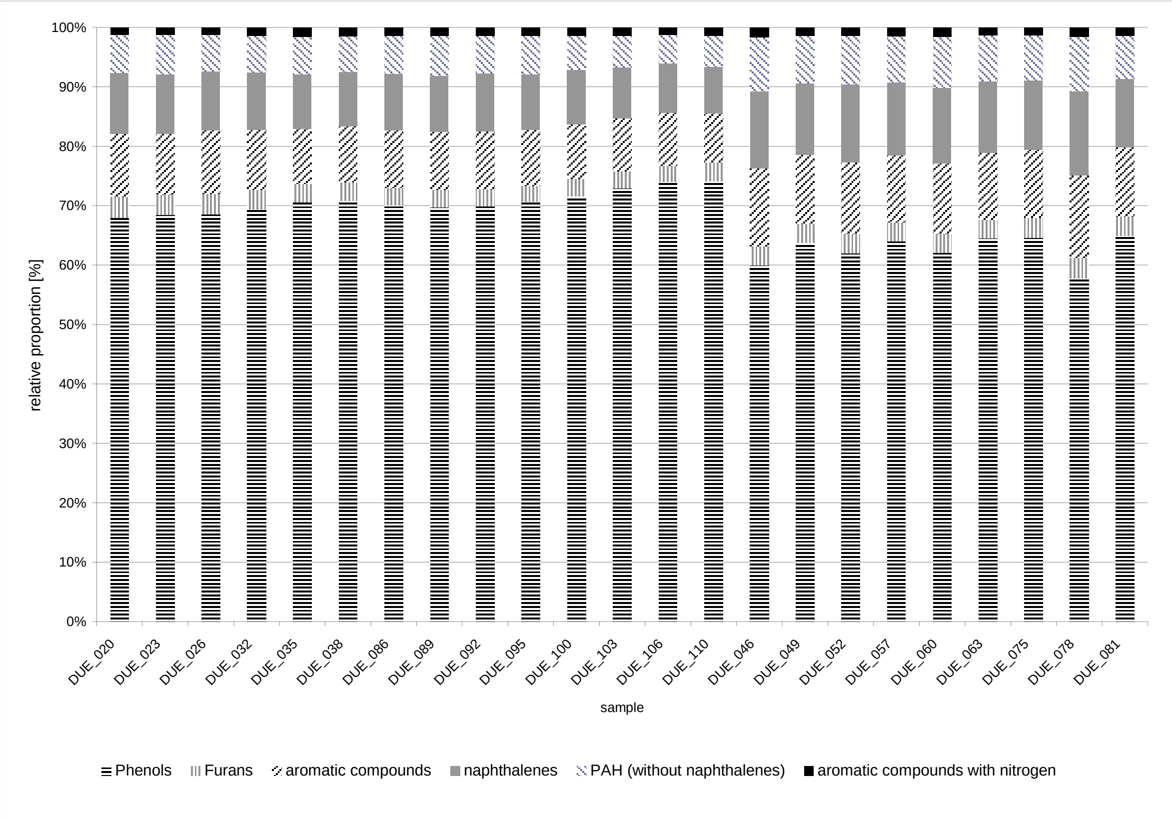

Figure 2: Relative proportions of group compounds of GC/MS tar

The pyrolysis gas mainly contains H_2, CO_2, CO, CH_4, trace amounts of larger gaseous organics compounds and water vapor.

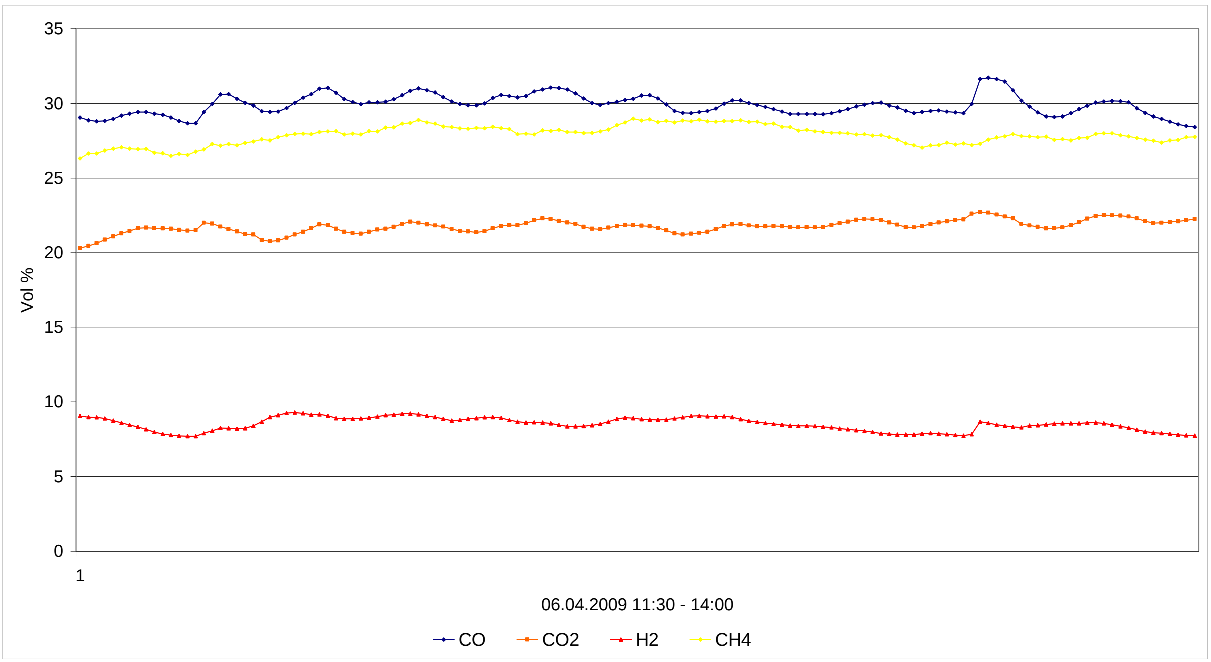

Figure 3: Pyrolysis gas composition

The water content results from the biomass humidity, about 10 % and from the reaction water. To control the water content, the water content of the used biomass should be in the range of 10 wt.%. The carbon content of the straw samples is approximately 48 wt. % (db) and the corresponding LHV by 17600 kJ/kg (db). Due to the process the carbon content in the char samples is enriched and rises to 67-76 wt. % (db). Therefore, the LHV of char samples rises to 26900-28500 kJ/kg (db)

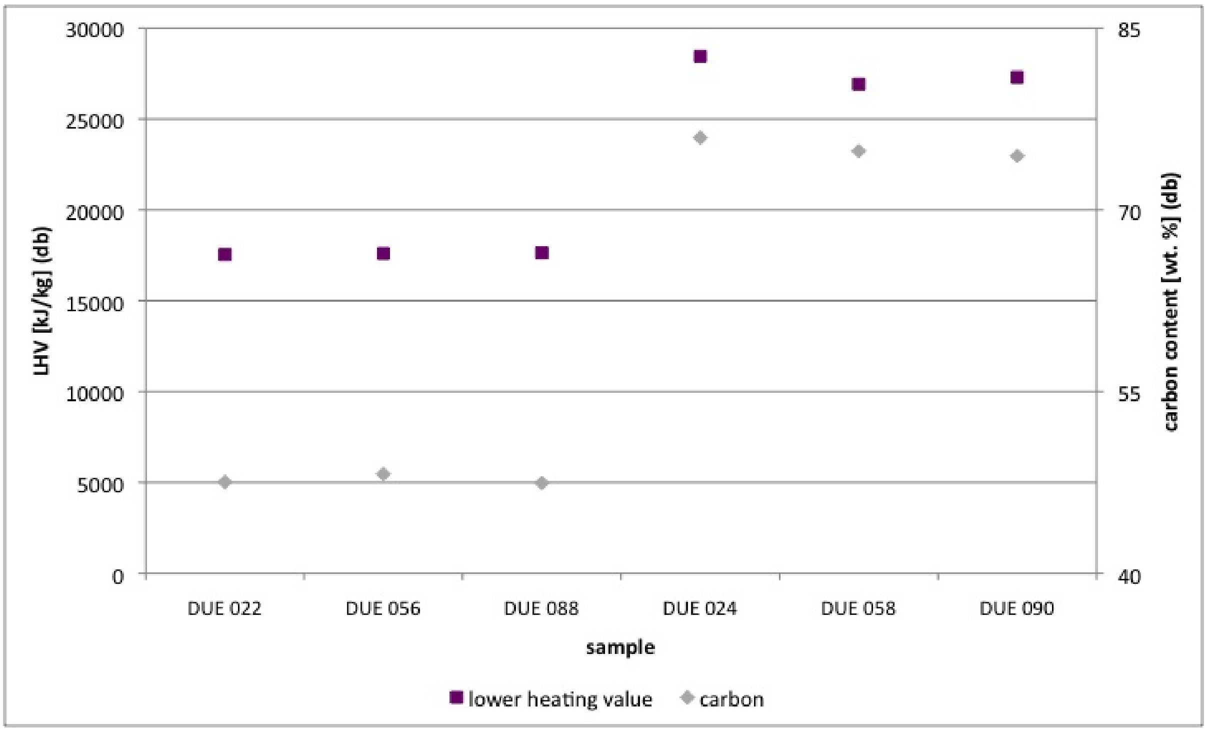

Figure 4: Carbon content and lower heating value of the straw and char samples

The pyrolysis process causes an enrichment of potassium, chlorine, sulphur, sodium and nitrogen in the char. This enrichment is wanted because those elements are partly removed from the pyrolysis gas. Especially chlorine, sodium, potassium and sulphur can lead to corrosion in the gas pipes as well as in the reactor and heat exchange surfaces. Hydrogen decreases in char samples because it is used in reactions during the pyrolysis process and can be found in the pyrolysis gas.

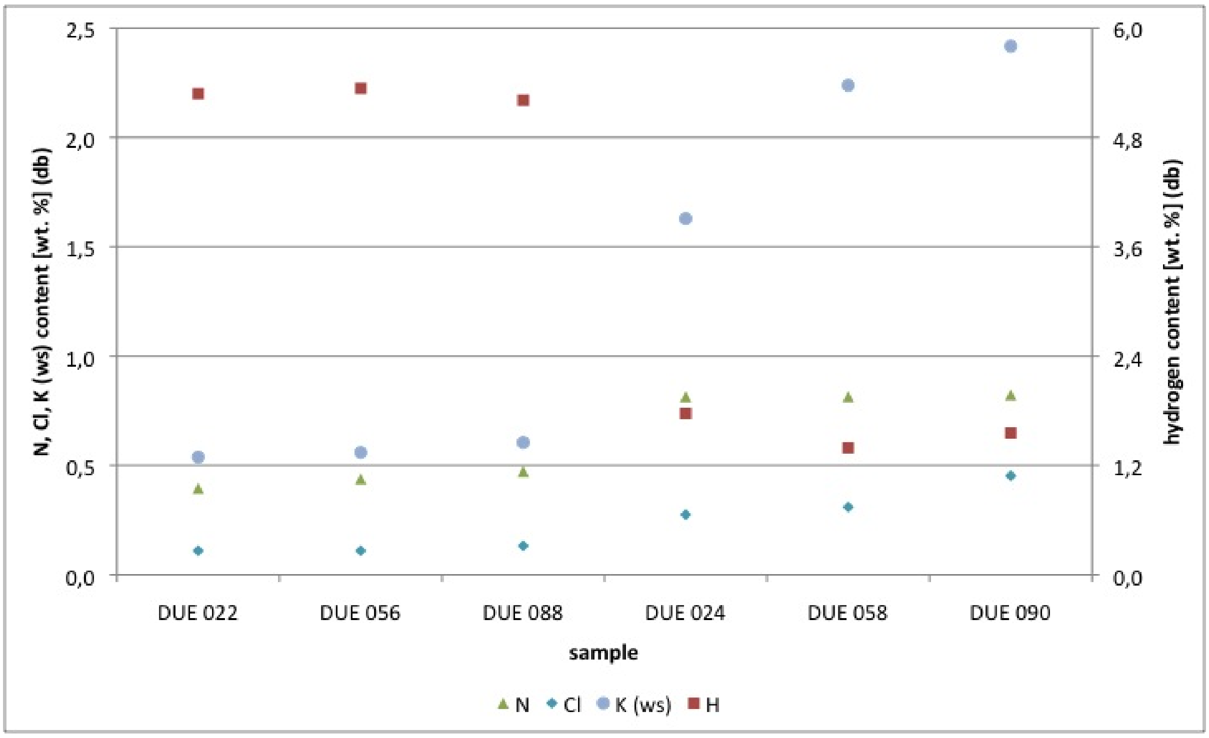

Figure 5: Elemental analysis of the straw and char samples (N, Cl, K ws, H)

The charcoal consists of carbon, volatile components, ash and partly tar. The content of carbon is one of the most important parameter for the quality of the charcoal, as well as the water content, ash content, elemental analysis, particle size, and energy density. All of the quality characteristics depend on the used biomass and the pyrolysis process as well as the purpose of use. Straw has a content of 79 wt. % (db) volatiles and char only 9 wt. % (db) (shown in Figure 6), which is reasonable to the devolatilization process of pyrolysis. Also displayed in this figure is the correlation of volatile components and ash content. The ash content in char is higher due to the enrichment of the mineral compounds in the char.

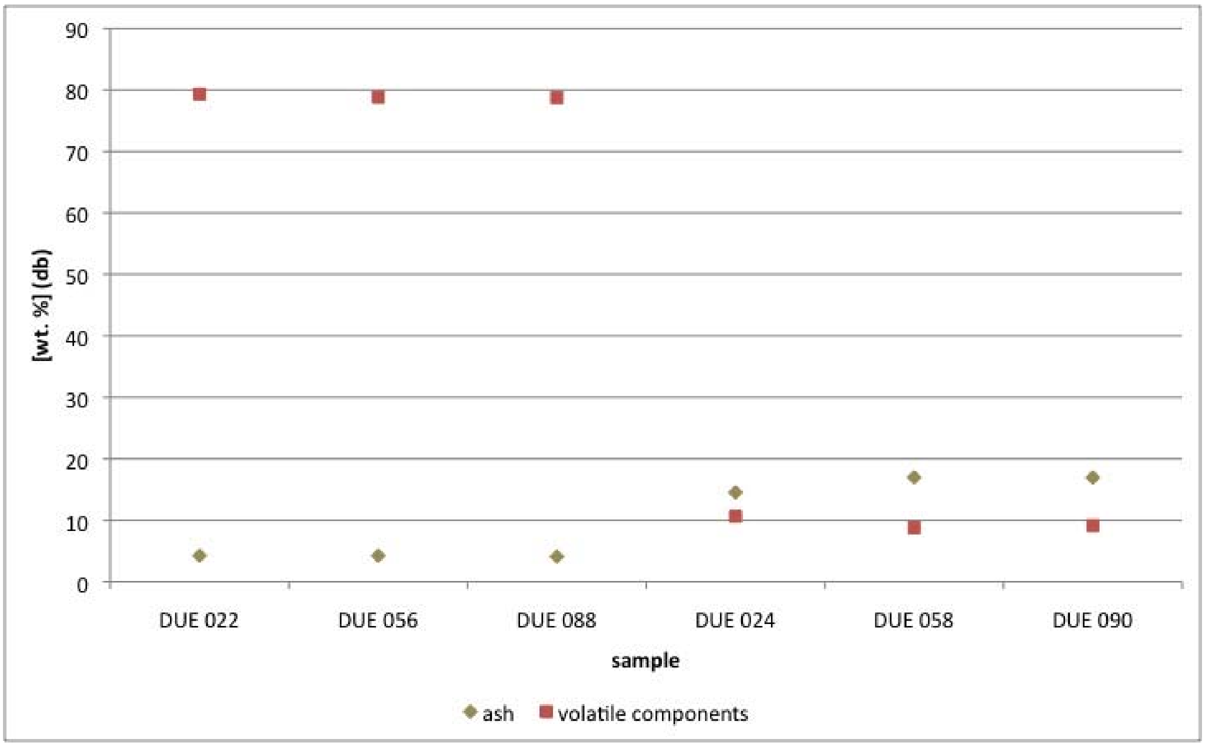

Figure 6: Ash and volatile components of straw and char samples

F. Conclusion

The findings of the pilot plant will deliver fundamentals for the development of an advanced pyrolysis model. Furthermore, the results will be the basis for a scale up to a 30 MW capacity. For an improved description of this highly complex process, more runs in the pilot plant need to be carried out in the future.

G. References

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H. Acknowledgment

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