VALORISATION OF LOW GRADE BIOMASS TO SUBSTITUTE FOSSIL FUELS IN A THERMAL POWER PLANT

M. HALWACHS\textsuperscript{1,3}\textsuperscript{*}, G. Kampichler\textsuperscript{2,3}, ST. KERN\textsuperscript{1,3} and H. HOFBAUER\textsuperscript{1,3}

\textsuperscript{1} Bioenergy 2020+ GmbH, Güssing, Austria
\textsuperscript{2} Energieversorgung Niederösterreich EVN AG, Maria Enzersdorf, Austria
\textsuperscript{3} Institute of Chemical Engineering, Vienna Technical University, Vienna, Austria

*\texttt{michael.halwachs@bioenergy2020.eu}, +43 664 5683 674, +43 3322 42 606 199

\textbf{Keywords}: pyrolysis, agricultural residues, power plant

\textbf{Abstract}

Minimizing carbon dioxide emissions whereas keeping up the high living standard of today is only possible by increasing the efficiency of energy consumption and the change to a mix of renewable fuels. Huge amounts of unused biomass in terms of agricultural residues like straw, that is a cheap and local feedstock, are often available. But as a reason of the high amount of corrosive ash elements (K, Cl, S), the residues are not suitable for co-firing in a thermal power plant. Therefore the feedstock is converted by low temperature pyrolysis into pyrolysis gases and charcoal. The aim of this work is to obtain fundamentals for an advanced pyrolysis model approach by the results of the pilot plant for co-firing the pyrolysis gases in a thermal power plant. A 3 MW pyrolysis pilot plant is being operated since 2008. For the process, an externally heated rotary kiln reactor with a design fuel power of 3 MW is used. Several mass and energy balances have been calculated based on measured plant data for different operating points of the pilot plant. The high amount of pyrolysis oil in the gas has positive effects to the heating value of the pyrolysis gases. As a reason of that, cold gas efficiencies of more than 70\% are possible. Based on these results, a scale up to a next scale pyrolysis reactor with a capacity of 30 MW\textsubscript{th} fuel input is currently investigated.
1- INTRODUCTION

The global warming due to the increasing CO₂ emission and dependency on fossil fuels, as well as the high-energy price level have resulted in an increasing demand in renewable energy sources. Biomass, as a renewable energy source, has the potential to contribute to the future energy mix in many countries. The desire of the conversion of biomass is to generate useful primary products. The choice of the conversion process depends upon the type and quantity of biomass feedstock, the desired form of energy, end use requirements, environmental standards and economic conditions. The two main processes to convert biomass into useful products are thermo-chemical processes and bio-chemical processes. Thermo-chemical processes include combustion, gasification, liquefaction, hydrogenation and pyrolysis. Bio-chemical processes are aerobic and anaerobic decomposition, which include the alcoholic and methane fermentation. 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 450-630 °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.

2- MATERIALS AND METHODS

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 pre-treatments 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] 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 to 0.8 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 occurs separately in a fluidized bed reactor.

Several analytical methods are used to get more insight about the behavior 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. Test runs were carried out at pyrolysis gas temperatures ranging from 450 to 630 °C. Variation of residence time and a broad range of different agricultural residues have been under investigation.

- Wheat Straw (indoor stored)
- Wheat Straw (field stored)
- Maize Straw
- Straw Pellets
- Sorghum Straw
- Reed Straw
- Palm Nut Shells
- Miscanthus Straw
- Waldviertler Energygras
- Grain Stillage

3- 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 40-200 g/Nm³. The actual high amounts of gravimetrical tars at pyrolysis gas temperatures ranging from 450 to 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 30-100 g/Nm³ 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. The tars formed from lignin are mostly substituted phenols, which explain the high amount of phenols. The lineage of phenols with the lignin tar formation is reasonable due to the aromatic likely phenol base structure of the lignin. The pyrolysis gas mainly contains H₂, CO₂, CO, CH₄, trace amounts of larger gaseous organics compounds and water vapor. The water content results from the biomass humidity 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 fuel samples is in the range of 42 to 53 wt. % (db) and the corresponding LHV ranges from 13500 to 19000 kJ/kg (db). Due to the process the carbon content in the char samples is enriched and rises to 45-84 wt. % (db). Therefore, the LHV of char samples rises to 16500-31500 kJ/kg (db)

![Figure 2: Carbon content and lower heating value of fuel and char samples](image)

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

![Graph](image)

Figure 3: Elemental analysis of fuel and char samples (S, Cl, Na)

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. The different agricultural residues have a content of 63 to 84 wt. % (db) volatiles and the char only 7 to 17 wt. % (db) (shown in Figure 4), 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.

![Graph](image)

Figure 4: Ash and volatile components of fuel and char samples
An important part of the work is the balance of mass and energy of the pilot plant, which is performed by the software package IPSEpro. This tool has been used for R&D projects at the Institute of Chemical Engineering for several years. As a result, new applications in the field of biomass-based energy systems have been developed. Because every model is based on the conservation of mass and energy, the validation of the measured data is also feasible. Comparison between reconciled values and directly measured values allows the localization of systematic errors. The simulation describes the actual plant operation best within the limits of the model structure and can be used as starting point for plant optimization. Several mass and energy balances have been calculated based on measured plant data for different operating points of the pilot plant. Pyrolysis oil to pyrolysis gas ratios are the results of variation of the plant parameters, like pyrolysis temperature, heat rate or residence time. The high amount of pyrolysis oil in the gas has positive effects to the heating value of the pyrolysis gases. As a reason of that, cold gas efficiencies of 70 % are possible.

![Figure 5: Calculated flows of pyrolysis gas/char/tar in [kW]](image)

4- CONCLUSIONS

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.

REFERENCES