GASIFICATION OF WET BIOMASS IN SUPERCRITICAL WATER. RESULTS OF PILOT PLANT EXPERIMENTS

N. Boukis, U. Galla, P. D´Jesus, H. Müller and E. Dinjus
ITC-CPV, Forschungszentrum Karlsruhe,
P.O. Box 3640, 76021 Karlsruhe, Germany; Tel: +49 7247 82 4825, e-mail: nikolaos.boukis@itc-cpv.fzk.de

ABSTRACT: Wet biomass reacts with water at supercritical water conditions to form a gas rich in hydrogen. The reaction of the organic substances with water proceeds at temperatures of 600 °C and pressures of 25 MPa at residence times in the order of 2 – 4 min with high space-time yields. Only small quantities of tar and soot are formed. Carbon forms CO2, - which can be separated by a step of water washing - and methane. Usage of efficient heat exchangers is possible under the high pressure reaction conditions. This permits the treatment of water – rich biomass without pre-drying. The consumption of electric power to generate high pressure is low, due to the low compressibility of the slurry. These factors lead to a high energy efficiency even for diluted feed. These facts have been experimentally tested with the pilot-plant VERENA which has a continuous flow of 100 kg/h and is dedicated for the process of biomass gasification in supercritical water.
Keywords: pilot plant, pressurized conversion, gasification, hydrogasification, hydrogen, methane, organic waste.

1 INTRODUCTION

Several streams of waste biomass and fresh plants available for the production of energy and fuels are not suitable for common gasification processes because of their high water content (>70 %). For classical gasification processes the biomass has to be dried, which is an energy and time consuming step. This can be avoided by gasification or liquefaction of biomass in near-critical or supercritical water.

First experimental results were published by Modell and Antal in the 70´s. Antal et al. reported (in later publications) [1] that the highest yield of hydrogen for the supercritical water gasification of sawdust and different starches is reached at high temperatures. Lee et al [2] reported total conversion of glucose at 700°C. Higher heating rates are reported to lead to higher gasification efficiencies, because the formation of tars and chars is inhibited [3, 4]. Hao et. al. reported that pressure has no influence on the gasification of glucose [5].

Diem et.al. showed, that at least in case of methanol in water solutions, the gasification reactions are catalyzed by the heavy metals of the inner surface of the reactor. [6, 7]. Reactors with an inner surface made of alumina lead to a poor gasification performance. A pre-oxidation of the inner surface of the reactor has been reported to enhance the reaction rate [8, 9].

Experimental results for the energy balance of the process were published last year [10]. There is a net output of energy for a diluted 10 wt % methanol in water solution. On the other hand is has been reported, that the efficiency of the heating system is important for a higher energy output. [11]

2 LABORATORY SCALE EXPERIMENTS

2.1 Experimental

The dependence of the yield of the supercritical water gasification of corn silage from the residence time has been measured at different temperatures. The experimental set-up used for these experiments can be seen in Figure 1 and has been described in [12, 13]. The biomass was diluted from 30 wt % dry organic matter (DOM) to 5 wt%. Also the size of the particles has been reduced in a two step procedure to less than 1 mm. The potassium concentration of the feed was high enough for high gasification yield (1500 ppm); no addition of potassium salts was necessary.

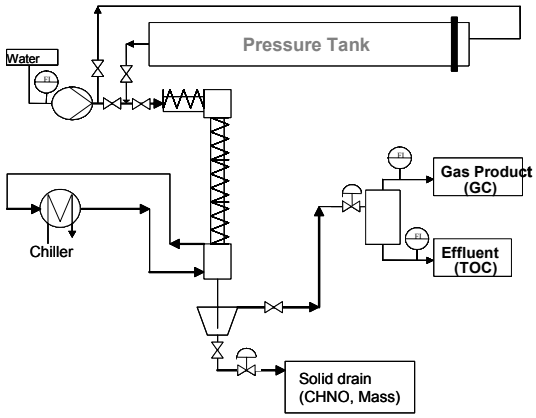


Figure 1: Experimental set-up for the laboratory scale experiments.

2.2 Influence of the temperature on the gasification of corn silage.

At any given temperature (see Figure 2), the gasification efficiency increases linearly with the residence time. When a certain value of gasification efficiency is reached, however, prolongation of the residence time did not influence the gas yield. This is

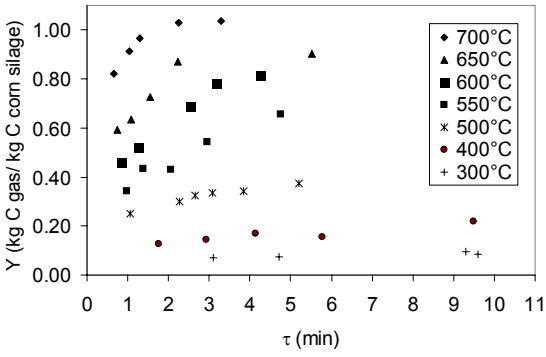


Figure 2. Gasification efficiency (Y) of corn silage at different temperatures at p = 25 MPa and a concentration (DOM) of 5 wt.%, as a function of the residence time.

probably due to the fact that corn silage consists of numerous compounds and some of them can not be gasified at the certain reaction temperature.

From the data of figure 2 is clear, that the gasification reaction has a yield higher than 50% at temperatures higher than 550 °C. The required residence time is in the order of 2 up to 3 min. Complete gasification is achieved at a temperature of 700 °C. The gasification yield at 650 °C and residence times longer than 2 min. is about 90 %. These conditions were chosen for the experiment in the pilot plant.

3 PILOT SCALE EXPERIMENTS

3.1 Description of the pilot-plant VERENA

The pilot plant VERENA (a German acronym for "experimental facility for the energetic exploitation of agricultural matter"), has a total throughput of 100 kg/h (max. 20 % dry biomass) and is in operation since 2003. The plant is designed for an operating pressure of up to 35 MPa and a maximum temperature of 700 °C. Common operation conditions are a flow rate of 50 or 100 kg/h, a maximal reaction temperature of 660 °C at a pressure of 28 MPa (see Figure 3).

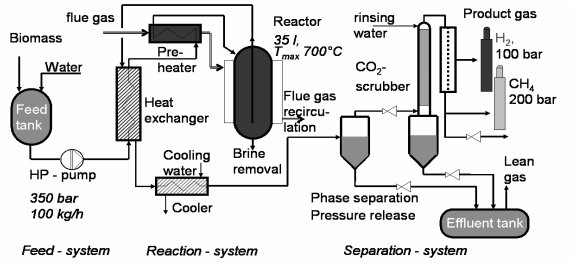


Figure 3: Pilot Plant for the gasification of wet biomass in supercritical water "VERENA": Simplified flow sheet.

The feed system is qualified for the handling of different educts, such as biomass, mud (including sewage sludge) and liquid educts. A measured quantity of the educt is transferred into the stirred preparation tank (volume 1.5 m³) which is connected to several mills. The water content of the feed and the maximum size of solid particles are adjusted to obtain a homogeneous feed, suited for pumping. The conditioned and analyzed educt is transferred to the stirred store tank (volume 3 m³). The feed is dosed by a mass-flow controlled high pressure metering pump to the reaction system. Improvements of the feed system enable the treatment of educts with a very high amount of fibrous matter such as corn silage. The particle size of these materials is reduced by a treatment with a cutting mill (preparation tank). Then follows a short-time treatment with a colloid mill, it results in a particle size less than 1 mm. It is expected that commercial plants with a 10 to 100 times higher flow rate will work even more reliable.

Important for the economics of the process is the low electrical energy consumption of the high pressure pump. For a flow rate of 100 kg/h and 28 MPa pressure the power demand is less than 2 kW_e for all pumps used for the process.

The educt flow passes a double-pipe heat exchanger with an exchange surface of 1.1 m^2 and is heated in counter current flow by the hot (T ≈ 600°C) effluent from the reactor. For operation with water (flow rate 100 kg/h) a heat transfer coefficient k = 700 $Wm^{-2}K^{-1}$ has been calculated. After several hundred hours of operation, some fouling occurs and the k – value decreases. The pre-heated educt is lead into the reactor, which is heated by externally generated flue gas. The reactor can be operated up to 700 °C and is divided into two parts. The first part is a tubular (9/16") reactor which acts primarily as a heat exchanger; the second part is a slim vessel (i.d. 110 mm, volume = 35 L) to guarantee the required residence time. The reactor is constructed as a down flow reactor. One feature of the VERENA plant is the separation of brines and solids via a third output from the lower part of the reactor. This helps to avoid clogging and to reduce fouling of the heat exchanger.

Under supercritical conditions, the gaseous reaction products are soluble in water and leave the reactor as a homogenous phase, pass the heat exchanger and a cooler. By cooling down the product, gases separate from the water phase. The two phases are separated and the pressure can be reduced alternatively in one or two steps. One separator is equipped with an integrated CO_2 scrubber. Here, the CO_2 content of the product gas is reduced by the addition of cold water. The product gas is relieved to the pressure required for further treatment. Via a level control, the water phase is passed on to a third separator, operating at ambient pressure, to remove lean gas and solids from the effluent. Then the effluent is led to a store tank.

The burnable gases can be used in different ways for energy generation or chemical reactions. In the VERENA plant the product gases can be filled up in high pressure bottles. The excess gas is passed to a torch and is burned.

3.2 Experimental

The corn silage used originated from the sort dodge. The original particles were up to several cm long. The Dry matter (DM) content was 36.7 wt. %. The composition of the DM was (all values in wt. %): C 44.3; O 42.8; H 6.3; N 1.05; K 3.2; Ca 0.38; Fe 0.05; Cl 0.74; Si 0.55; S 0.3; P 0.3. Dilution with water by a factor of 4 resulted in a concentration (DM) of 9.2 wt. %. A cutting mill has been used to reduce the size of the biomass particles down to a few mm. Some hard and almost spherical particles with a diameter of less than 3 mm could be detected in the well flowing feed slurry. This could affect the valves of the high pressure pump. To prevent this a second milling step with a colloid mill has been executed. After this treatment 84 % of the total mass was smaller than 0.5 mm. The organic carbon concentration of the feed was 3.96 wt. % (see Table I) and the pH 3.7 (due to the silage step). The operation conditions in the experiment with corn silage were: Feed rate 50 kg/h, T_{max}= 610 °C, p = 28 MPa,, mean residence time= 4 min and the CO_2 stripping was in operation.

Pyroligneous acid is a by-product of the charcoal production. In industrial charcoal production, pieces of wood are carbonized (absence of oxygen) in large-volume retorts. Pyrolysis products of dry beech wood charcoal production are charcoal (34 wt. %), gas (16 wt.%), pyroligneous acid and tar (24 wt. %) and water. The gaseous carbonization products are hydrogen, methane and ethylene. The main component of pyroligneous acid is water (about 75 wt. %). The organic matter consists of acetic acid, formic acid, methanol, acetone, methyl acetate and wood tar. For the experiment

in the pilot plant the original material has been diluted by a factor of 3. The total organic carbon (TOC) of the feed was 3.73 wt. %. The concentration of acetic acid (main component) was 3.21 wt. %. The sulphur concentration was 0.45 wt % and the chlorine concentration was 0.04 wt %. The pH was 2.46. Some potassium salts were added to the feed, the [K] was 111 ppm. The operation conditions of the experiment with pyroligneous were: Feed rate 50 kg/h, T_{max}= 620 °C, p = 27 MPa, mean residence time= 4 min.

The experiment with ethanol has been performed with a solution 14.4 wt % with 100 ppm [K].

3.3 Energy balance.

Data for the energy balance of the process were measured in experiments with CH_3OH solutions. (p = 28 MPa T_{max} ~ 600 °C, flow rate = 90 - 100 kg/h and τ = 1.9 min. The electric power demand was 2 kW_e -with CO_2 removal 10 kW_e. As you can see in Figure 4 at a concentration of 10 wt % the lower heating value of the product gas is higher than the energy consumption. Additional thermal energy of about 11 kW_{th} at a temperature level of about 150 °C can be gained from the cooler.

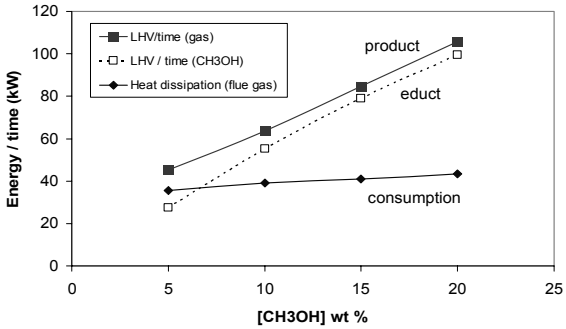


Figure 4: Lower heating value of the product gas and the methanol feed at different methanol concentrations compared with the heat dissipation of the heating flue gas (consumption).

The original data for these calculations will be published in [14].

3.4 Results of the gasification step.

After the time consuming feed preparation, the corn silage slurry could be pumped easily. The quite low flow rate of 50 kg/h could be kept constant during the whole experiment. The pressure was 28 MPa. During the run with corn silage the brine removal from the lower part of the reactor was activated. This device (see also [15]) is operated discontinuously with short duration but high flow rate. About 2 kg/h brine were removed in this way. The operation of the heat exchanger did not show fouling. This is an indication of the effective removal of solids from the lower part of the reactor.

The composition of the gas is listed on the right column in Table I. As comparison results from the gasification of pyroligneous acid are listed too. The comparison of the gas composition is surprising. The slurry from the corn silage consists of small particles of plant matter.

The pyroligneous acid consists of soluble or liquid tar like components. The main component is acetic acid. The similar composition of the product gases (see Table I) is an indication that during the short time (several sec) required for heating up the feed stream, the biomass decomposes and forms –before the gasification reaction- intermediate degradation products similar to the components of the pyroligneous acid.

Table I: Feed and product gas for the experiments in the pilot plant VERENA for two experiments.

		pyroligneous acid	corn silage
[C] feed	[g/kg]	37.4	39.6
gas flow	[Nm³/h]	3.07	2.53
H2	[Vol-%]	36.36	31.56
CH4	[Vol-%]	31.02	28.01
CO	[Vol-%]	0.48	0.47
CO2	[Vol-%]	27.42	27.76
C2H6	[Vol-%]	3.24	6.76
C2H4	[Vol-%]		0.46
C3H8	[Vol-%]		2.13
C3H6	[Vol-%]		0.51
N2	[Vol-%]		2.33

On the other hand the carbon gasification yield in the case of pyroligneous acid is 97 %, in the case of corn silage only 90 %. The residual 10 % of carbon were mainly water soluble or oily compounds. The carbon balance could be closed in both cases. This means that some of the components of the corn silage exhibit a slow gasification kinetic. In any case the result of the experiment with corn silage in the pilot-plant are well comparable with Figure 2 (lab scale experiments).

The gas composition in the case of a 14.4 wt % ethanol shows more hydrogen (see Figure 5).

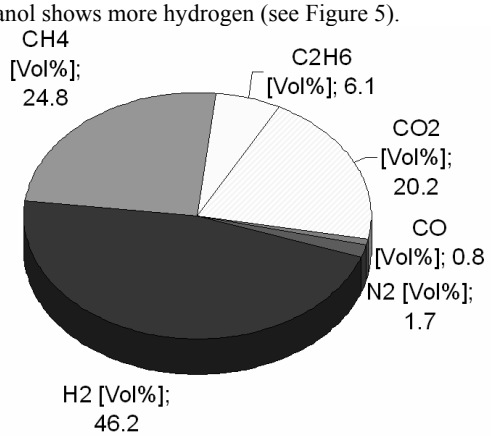


Figure 5: Hydrothermal gasification of a 14.4 wt % ethanol solution at 625°C, 28 MPa pressure, flow rate 100 kg/h and a mean residence time of 2 min (without CO_2 stripping).

Since the experimental conditions were not exactly the same (concentration, mean residence time) it is not possible to assign this difference to the shorter residence time or to the more simple chemical structure of the ethanol. The carbon gasification rate was 99 %.

The experiment with corn silage had the highest load of inorganic salts of all other previous experiments. It is well known that inorganic salts precipitate at supercritical temperatures. Presumably this occurred during this experiment too. The pre-heater of the plant

has been plugged after 3.5 h of operation.

3.5 CO_2-separation.

After filling the wash-column for the CO_2 separation from the product gas with Pall rings, it has been operated during the gasification experiment with corn silage. The aqueous effluent (and the CO_2 part which is dissolved into it) is separated from the product gases in the first stage of the pressure regulation system. In the second stage, residual CO_2 is separated from the other gaseous reaction products by addition of water at ambient temperature in a high pressure scrubber column. The pressure of the first step was 28 MPa, of the second step 15 MPa. The gas flow was 2.5 Nm^3/h and the water flow 80 l/h (T ≈ 20 °C).

Separation of carbon dioxide was highly effective (from 32 vol % down to 1 vol %). Less than 10 % of the total amount of hydrogen has been washed out in the scrubber column during the washing step (see Figure 6).

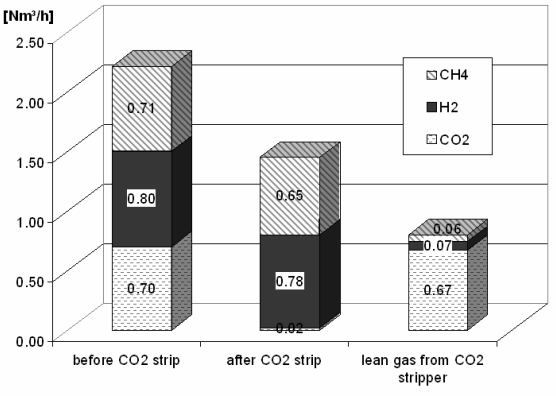


Figure 6: Concentration of the main components of the product gas, before and after the CO_2 separation treatment. The lean gas contains the separated gases after release of the water solution at normal pressure.

Also the losses of methane are low. The amount of water used was much higher than necessary. The main target in this first operation of the column with normal gas flow was to separate effectively the CO_2 and not to optimize the water consumption. A theoretical approximation (solubility coefficients from [16], water flow 80 kg/h at p = 15 MPa] of the composition of the lean gas gives the following values: H_2 0.07 Nm^3/h; CH_4 0.11 Nm^3/h, CO_2 2.89 Nm^3/h. The comparison with the experimental values on Figure 6 reveals, that the technical system applied works well and that the amount of water used can be reduced by a factor up to 4. A reduction of the flow rate will result in much lower hydrogen and methane losses.

4 CONCLUSIONS

The hydrogen production from wet biomass in supercritical water has been demonstrated with ethanol, pyroligneous acid and with corn silage. The carbon gasification yield is 97-98 % in the case of ethanol and pyrolygneous acid and 90 % in the case of corn silage. In all cases the mass balance of the chemical elements could be closed. The CO_2 can be washed out just by addition of compressed water from the product gas. The resulting combustible gas consists half of hydrogen and half of hydrocarbons, mainly methane with some ethane and propane. Further work will be focused on the application of improved process layouts to prevent plugging and to enhance reliability and economics of the process.

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