BIOMASS GASIFICATION IN SUPERCRITICAL WATER. EXPERIMENTAL PROGRESS ACHIEVED WITH THE VERENA PILOT PLANT.

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ABSTRACT: At supercritical water conditions (T ≈ 600 °C, p ≈ 28 MPa) biomass reacts with water to form a combustible gas rich in hydrogen and methane. Hereby, hydrogen from biomass as well as from water is gained. Usage of efficient heat exchangers leads to a process of high efficiency. Water-soluble salts will form solids under supercritical water conditions. Present work focuses on an improved process layout in order to avoid plugging of the tubes due to the formation of inorganic solids during the process. Two innovations were made. I) A process layout with a heat exchanger divided into two parts on the feed side. The biomass is heated up to sub-critical temperatures and mixed with water (heated at high supercritical temperatures) in the reactor space II) Due to the flow direction and gravity, solids formed in the reactor space will be accumulated in the lowest part of the reactor and will be removed from the process. The clean main product stream is directed to the upper side and passed to the heat exchanger. This process scheme helped to avoid any disruption of the flow during the planned operation time of 10 h. The hydrogen concentration was high (77 vol. %), after an integrated CO_2 removal. The concentrated product gas is provided at high pressure (up to 20 MPa).
Keywords: Hydrogen, gasification, pilot plant

1 INTRODUCTION

Wet waste biomass streams (slurries, sludge) 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 the gasification of biomass in near-critical or supercritical water.

At supercritical water conditions (T>374 °C, p>22.1 MPa) biomass reacts with water to form a combustible gas rich in hydrogen and methane. Hereby, hydrogen from biomass as well as hydrogen from water is gained. Thus, water is an additional hydrogen source. Typical reaction conditions of this process - also known as hydrothermal gasification - are temperatures of 600 °C and pressures of 300 bar [1-3]. The process does not require heterogeneous catalysts. At high temperatures, complete gasification is reached [4-6]. Alkali salts always present in biomass play an important role as catalysts [7-9]. Use of catalysts can reduce the required reaction temperature, but the stability of the catalyst is some times not high enough [10-11].

The CO_2 formed can be separated from the product gas just by addition of water in a wash column. Reactions are fast and almost complete gasification with high space-time yields has been achieved. Usage of heat exchangers is possible at supercritical water conditions. Compression work is low. This leads to a high efficient process even for educts with high water content. The process of biomass gasification in supercritical water does not require heterogeneous catalysts to produce hydrogen. This is an advantage for the treatment of biomass and organic wastes, which commonly contain sulphur, chlorine and other components, which can poison the catalysts applied in other technologies.

Most important for commercial application is the possibility to gasify waste biomass from industrial processes as the wine, beer, ethanol, sugar production or sewage sludge from enzymatic processes. These feeds will be available in higher quantities in an industrial installation, pre-treated and cost free.

2 EXPERIMENTAL

2.1 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 designed for an operating pressure of up to 35 MPa and a maximum temperature of 700 °C. Usually the plant is operated at a flow rate of 100 kg/h and a maximal reaction temperature of 660 °C at a pressure of 28 MPa.

The feed system is qualified for the handling of common biomass with larger particles / pieces. The particle size of these materials is reduced by a treatment
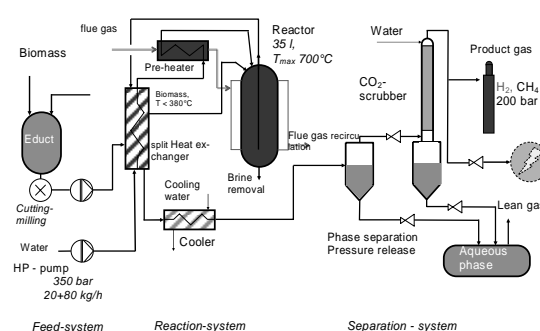

Figure 1: Process scheme applied for the experiment

with a cutting mill. A short-term treatment with a colloid mill follows, which results in a particle size of less than 1 mm. The water content of the feed is adjusted to obtain a homogeneous feed suited for pumping. The feed is dosed into the reaction system by a mass flow controlled, high-pressure metering pump 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 down-flow reactor. A small size tube (9/16") takes the product mixture from the lower part of the reactor and leads it through the head of the reactor to the heat exchanger. A feature of the VERENA plant is the separation of brines and solids via a third output from the lowest part of the reactor (see Figure 1). This helps to avoid clogging and to reduce fouling of the heat

exchanger.

The process scheme applied provides a moderate heating of the biomass up to the critical temperature in a small part of the heat exchanger. This helps to avoid precipitation of inorganic salts. A second stream of pure water uses the largest part of the heat exchanger and the pre-heater to reach high temperatures. Both streams are mixed in the top of the reactor (see Figure 1). The heating of the biomass up to the reaction temperature takes place in the down flow reactor by mixing it with the hot stream of water. The salts will be transported downwards by gravitation and flow to the lowest part of the reactor and will be separated from the reaction system by the brine removal system.

Under supercritical conditions, the gaseous reaction products are soluble in water and leave the reactor as a homogeneous 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. The scrubbing column for CO_2 separation from the product gas is filled with Pall rings and has been operated during the gasification experiment with corn silage and ethanol. Here, the CO_2 content of the product gas is reduced by the addition of cold water. The product gases can be filled into high-pressure bottles. The excess product gas is expanded to the pressure required for further treatment. Via a level control, the water phase is passed on to a third separator run at ambient pressure to remove lean gas from the effluent. Then, the effluent is led to a store tank.

2.2 Process parameters applied

Experiments with pure ethanol and with a slurry from corn silage and ethanol were performed. The corn silage used had the composition (in wt.% of dry organic matter DOM): C = 43.4; O = 46.7; H = 6.17; N = 1.02; K = 0.98; S = 0.93; Si = 0.35; Ca = 0.2; P = 0.14; Cl = 0.13; Fe = 0.01. The pre-treatment was cutting of the solid particles with a macerator and milling by a colloid mill. The process parameters are listed in Table I.

Table I: Preset process parameters for the experiment with a pure ethanol solution and a slurry of corn silage and ethanol.

	Ethanol	Corn silage /Ethanol
c Ethanol (wt %)	52,2	11
c DOM (wt %)	-	11
c K^+ (mg/L)	285	1784
Flow rate feed (kg/h)	20	20
Flow rate water (kg/h)	80	80
T feed (°C)	347	360
T water (°C)	599	620
T reactor	545	540
p (MPa)	28	28
t_R (min)	1.75	1.78
CO2 strip		
Water flow (L/h)	100	44
p (MPa)	17.6	17.4
T (°C)	25	26

3 RESULTS

3.1 Experiments with ethanol

For the first experiment with the new process scheme a diluted ethanol solution has been applied. Due to the rather low temperature of the reactor (545 °C) the C-gasification yield was low, only 58 %. The flow rate of the product gas was 14.12 Nm^3/h. The composition of the gas is shown in Fig. 2.
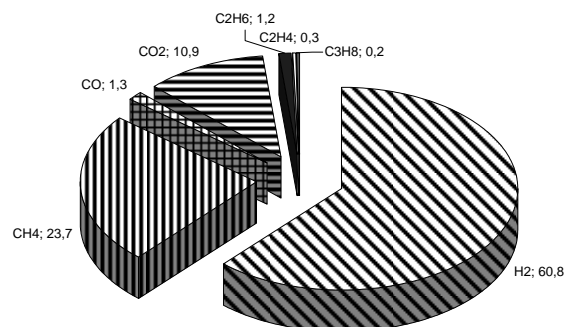

Figure 2: Composition of the product gas (vol. %) from the experiment with ethanol. Only partial CO_2 separation achieved. Flow rate feed = 20 kg/h, $[C_2H_5OH]$ =52,2 wt.%; Flow rate water = 80 kg/h, $T_{reactor}$ = 545 °C, p = 28 MPa, C-yield = 58 %.

The total amount of CO_2 was too high for the CO_2 washing column installed in the VERENA plant. The CO_2 separation was not complete. To compare these values with other previously published the CO_2 amount has been deducted from the product gas and the concentration of the other gases proportionally enhanced to give a sum of 100 % (see. Fig. 3).
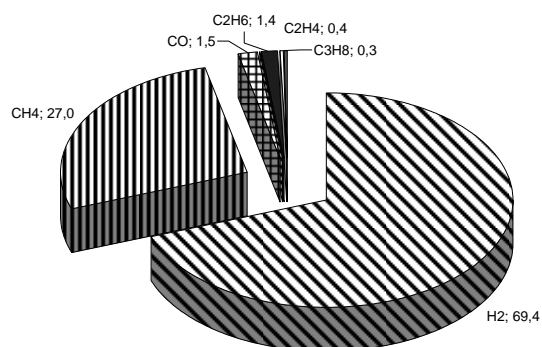

Figure 3: Calculated composition of the product gas (vol. %) without CO_2 (experimental values from Fig. 2)

3.2 Experiments with the corn silage / ethanol sludge

During the second experiment a sludge of corn silage has been used. Careful feed preparation is necessary to perform experiments with continuous flow under high pressure and solid containing biomass. Depending on the texture of the solid particles of the biomass cutting or milling or both are applied. With the corn silage used as

feed the resulting slurry showed high viscosity and had to be diluted to become pump able. To reach a higher concentration of organic matter for the first experiment ethanol was added to the feed solution. The final feed slurry had a concentration of corn silage of 11 % DOM and an ethanol concentration of 11 wt. %.

In former experiments with corn silage plugging occurred. It is well known that inorganic salts precipitate at supercritical temperatures. Presumably this occurred during a former experiment, too [3]. The preheater of the plant has been plugged after 3.5 h of operation.
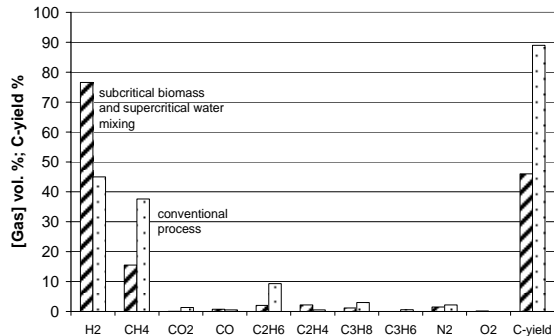

Figure 4: Composition of the product gas from the new and the conventional process scheme after the CO_2 separation. Flow rate feed = 20 kg/h, DOM = 11 wt. %, $[C_2H_5OH]$ =11 wt.%, Flow rate water = 80 kg/h, $T_{reactor}$ = 540 °C, p = 28 MPa, C-yield = 46 %.

In this experiment, the modified process scheme helped to avoid any disruption of the flow during the planned operation time of 10 h. The new process scheme provides a moderate heating of the biomass up to the critical temperature (see Table 1) in the heat exchanger.

This helps to avoid precipitation of inorganic salts. The heating up to the reaction temperature takes place in the down flow reactor by mixing with a hot stream of water. The salts will be transported down to the lowest part of the reactor and will be separated from the reaction system by the brine removal system (see Fig. 1).

The composition of the product gas is plotted in Figure 4. The flow rate of the product gas was 3.86 Nm^3/h, the CO_2 separation was complete. The comparison with the data from the conventional process does not enable theoretical conclusions since too many parameters were changed. The older data (see [3]) were measured at a reaction temperature of 610 °C and a mean residence time of 3.2 min. Also the feed used in the older experiment (conventional process) was different: it was a 9.2 wt. % corn silage slurry with out ethanol.

3.3 Influence of the reaction temperature.

The reaction temperature is known to have a determining influence on the C- gasification yield [5]. This has been confirmed in a series of experiments with a feed of ethanol also with the new process scheme (see Fig. 5).

On the other hand the influence of the reaction temperature on the selectivity of the reaction towards hydrogen is not pronounced (with an ethanol feed solution, see. Fig. 6).

The comparison of the data on Fig. 4 (although difficult) confirm also the crucial effect of temperature on the reaction yield. On the other hand the $[H_2]/[CH_4]$ ratio is almost 5 (see Fig. 4) with the new process

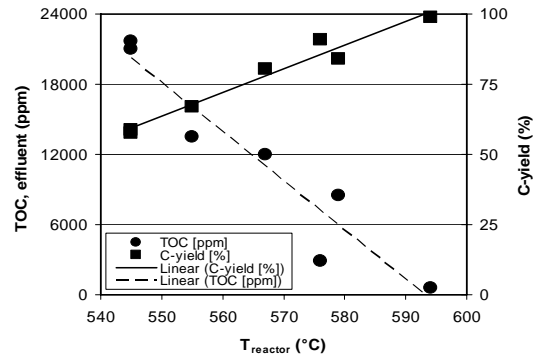scheme, compared to 1.2 with the conventional process

Figure 5: TOC and C-yield as a function of the reaction temperature. Total flow rate = 80 – 100 kg/h, $[C_2H_5OH]$ =8 – 12 wt. % in the reactor space, mean residence time 1.6 – 2 min.

scheme with only one feed stream. This tendency has to be confirmed in future experiments with higher reaction temperatures and other feeds. Now is not clear if this is due to the different process scheme or to the fact that only half of the total organic matter has been gasified. The experiment with pure ethanol as feed (see Fig 3 and 6) resulted in an small increase of the $[H_2]/[CH_4]$ ratio compared to the values published in [3].
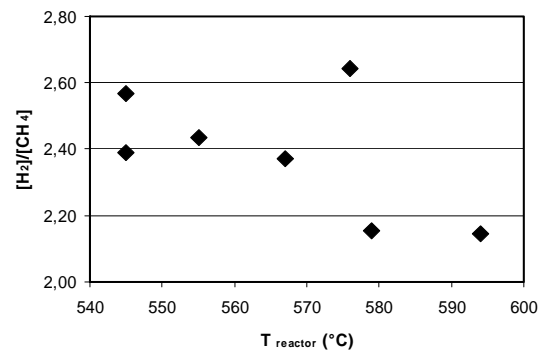

Figure 6: $[H_2]/[CH_4]$ ratio as function of the reaction temperature. Total flow rate = 80 – 100 kg/h, $[C_2H_5OH]$ =8 – 12 wt. % in the reactor space, mean residence time 1.6 – 2 min.

4 SUMMARY
- Pilot plant tests with the "VERENA" facility confirmed the high carbon gasification yield at high temperatures and showed a high energy efficiency of the process even for diluted educts (wet biomass). The hydrogen production from wet biomass in supercritical water has been demonstrated with ethanol and corn silage.
- The carbon gasification yield of ethanol is 99 % at $T_{reactor}$ = 594°C. The CO_2 has been washed out from the product gas just by addition of compressed water. By mixing the biomass (sub-critical temperature) with water (supercritical temperature) in the reactor space a steady operation during 10 h has been established.
- The hydrogen concentration was 77 vol. % . The C-gasification yield depends on the reaction temperature in the range of 540 - 600 °C.
- Further work will be focused on the application of the improved process layout at higher reaction

temperatures.

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