Production of Hydrogen and Methane from Biomass in Supercritical Water

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Summary

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. The CO_2 formed can be separated from the product gas by a water wash column. Reactions are fast and almost complete gasification with high space-time yields can be achieved. Usage of heat exchangers is possible at supercritical water conditions. Compression work is low since only a water slurry has to be pressurized. This leads to a very efficient process also for educts with high water content.

Systematic experiments with corn silage in laboratory scale equipment show the dependence of gasification yield from temperature. Complete gasification is achieved at 700 °C, with residence times up to a few minutes. Experiments in the new 100 kg/h continuous flow plant dedicated for the process of biomass gasification in supercritical water (acronym VERENA) show high thermal efficiency (~ 80%) for diluted feed streams (~ 10 wt% OM).

Introduction

For classical thermo chemical gasification processes under ambient pressure the biomass has to be dried, which is energy and time consuming step. A substantial part of the biomass available for the production of energy and fuels is not suitable for common gasification processes because of its high water content (>70 %). Several waste biomass streams and fresh plants belong to this category. The drying step can be avoided by gasification (or liquefaction) of biomass in near-critical or supercritical water. Compared to other biomass energy conversion technologies, supercritical water gasification (SWG) is the most efficient one for biomass with high moisture content [Yoshida2003]. Calzavara et al. (2005) evaluated the supercritical water gasification process for hydrogen production. They found out that the overall energy yield reached 90 % with energy recovery.

First experimental results were published by Modell, Yu and Antal (1985; 1993; 2000). Maple wood sawdust quickly decomposed in supercritical water to tars and some gas without formation of char. At temperatures higher than 600° C and at pressures higher than the critical pressure of water (22.1 MPa), the products are a burnable gas containing hydrogen, methane, carbon monoxide, carbon dioxide and some tar. Antal reported the complete gasification of biomass feeds (sugar cane bagasse, sewage sludge, corn- and potato starch gels, wood sawdust and potato wastes) using a carbon catalyst at temperatures above 600° C. Almost no tar or char products could be detected in the liquid effluent of the reactor. A product gas with high hydrogen concentration (up to 57 mol %) and gas yields of 2 L/g could be achieved. A high gasification yield at 650° C for the reaction of grape trash with a high surplus of supercritical water and without catalyst is described in (Boukis, 2002; Boukis2003). Hydrogen is the main component (≈ 70 %) of the burnable gas, the coke like residue amounts to about 5 %.

A lot of experimental work has been done to study the reaction of model compounds (Kruse, 2000). The Biomass Technology Group of the University of Twente has developed a pilot-plant (10 l/h) and a capillary screening technique to improve the supercritical water gasification of glucose (Potic, 2002). The carbon gasification efficiency increases asymptotically from 20 to 80 % within a temperature range of 460-700 °C.

Lee et al (2002) investigated the influence of temperature in the range of 510-750°C. They obtained total glucose conversion at 700°C. Also the heating rate influences the gasification of biomass in supercritical water. Higher heating rates lead to higher gasification efficiencies, because the formation of tars and chars is inhibited (Sinag, 2004; Matsumura, 2004).

Hao et al. (2003) studied the supercritical water gasification of glucose. They found out that pressure has just a small effect on the glucose gasification efficiency and the fraction of the gas product. Matsumura et al (1997) investigated the supercritical water gasification of coconut shell activated carbon. They found that changing the pressure from 25.5 to 34.5 MPa does not influence the gas composition. Other authors found out that a decrease of pressure leads to an increase of hydrogen formation (Kruse, 2000).

As feedstock of the supercritical water gasification process, two kinds of educts are considered: organic waste and energetic plants like corn. Corn is one of the most cultivated plants all around the world. It is adapted to almost any climate and its cultivation does not require any extreme conditions. Corn has a high energy content and high organic matter yield (per hectare) (Scheffer, 2000). Corn silage is chemically stable; it does not degrade and maintains its properties over long periods of time. For these reasons corn silage is available as feedstock for gasification during the whole year. Because of these advantages, corn silage is a feedstock suitable for the supercritical water gasification process and is investigated in the present work.

Experimental Method

The hydrogen and methane production from wet biomass has been studied in laboratory experiments to measure gas composition and the yield of carbon gasification and also in experiments in the pilot plant VERENA, to establish mass and energy balances.

At first the biomass is chopped to a size of less than 1 mm with different devices. Fibers can be as long as 3 mm. To conduct experiments at very low flow rates (less than 2L/h) the separation of the solid particles of the biomass from the water in the tubing and the heads of the pumps has to be avoided. A suitable method is the usage of xanthan as thickening agent. Xanthan was also gasified under the reaction conditions. Its concentration in the reaction mixture was 0.25 wt.%, this was the lowest concentration necessary to prevent separation of biomass and water. In the experiments in the pilot plant, the use of xanthan can be avoided. Instead of that a constant mixing of the feed and a high flow rate can be applied. The amount of water added depends on the desired concentration of the mixture and the dry matter content of the biomass (DOM). The elemental composition of the corn silage used in this work is:

Table 1. Elemental composition (in wt.% of dry organic matter) of corn silage

C	O	H	N	K	S	Si	Ca	P	Cl	Fe
43.40	46.70	6.17	1.02	0.98	0.93	0.35	0.20	0.14	0.13	0.01

Laboratory scale apparatus

Well established high-pressure equipment was used to investigate the gasification of corn silage. The reactor material was nickel base alloy Inconel 625. The reactor wall was treated once with a solution of H_2O_2 in water (3 wt.%) at 600 °C and 25 MPa for about 50 h after installation, according the procedure proposed in (Boukis, 2003).

The first experiments were performed with a continuous flow reactor (1700 mm long, 8 mm inner diameter) which was placed horizontally. Plugging of the reactor and uncontrolled convection of the fluid in the reaction tube made us change the flow direction and to install a down-flow reactor (1000 mm long and 8 mm inner diameter) with a preheater (250 mm long and 8 mm inner diameter). The reactor was heated up to a maximum reaction temperature of 700 °C by heating coils. The equipment included several temperature control units.

Temperature profiles were measured in order to optimize the set values of each heating device. The connections were cooled down by two chillers. The set up is illustrated in Fig. 1.

Pumping of biomass slurries at low flow rates was and still is a challenge. This challenge has been overcome with a pressure tank (volume >3 L) to store the prepared biomass. A common high pressure water pump drives a piston installed inside the pressure tank in order to seal the biomass from the clean water. The pressure tank was charged with the prepared biomass. The fermentation of the solution led to the agglomeration of particles and, consequently, plugging of the feed system was observed. To prevent the fermentation of the biomass during the summer time, the tank was cooled down to less than 10 °C.

Pressure was controlled by a back-pressure regulator (Tescom). After the expansion, the products were separated in two phases: Liquid and gas. The separation took place in a glass recipient, where sampling of the gas and the liquid phases occurred.

Usually each experiment lasted 5 hours at constant conditions. The steady state was reached within 2 hours (depending on the flow rate). After the steady state had been reached, gas and liquid samples were taken. For each experiment, at least five gas and liquid samples were analyzed to obtain a representative average. After each experiment the inner surface of the apparatus was cleaned with highly pressurized water

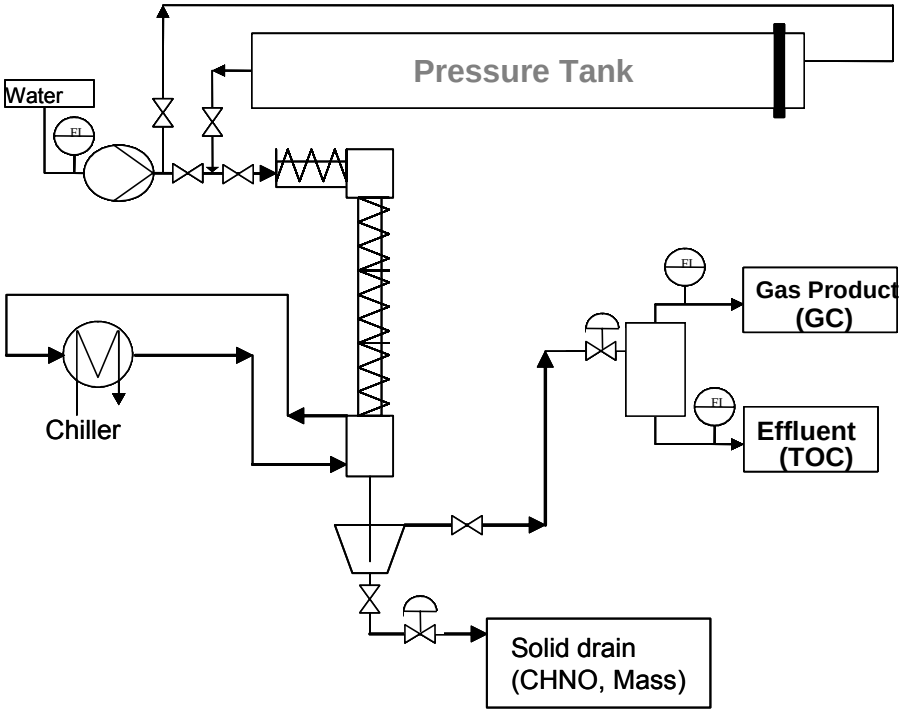

Figure 1: High-pressure laboratory equipment for SCWG

Gas composition was measured with a GC HP 6890 with two columns (80/100 Hayesep Q, 2 m long and 60/80 Mole sieve 5 °A, 4 m long), one for H_2 and the second one for CO_2, hydrocarbons, and helium as carrier gas. Concentration was measured by a thermal conductivity and flame ionization detector which were connected in series. The total organic carbon (TOC) and total carbon (TC) contents in the reactor liquid effluent were determined with a TOC analyzer (Rosemount Dohrmann DC-190). One gas flow meter (Ritter) and two balances (Sartorius) were used to estimate the educt, gas product, and the aqueous effluent flows.

Description of the Pilot-plant VERENA

The pilot plant VERENA (a German acronym for "experimental facility for the energetic exploitation of agricultural matter", see Fig. 2), has a total throughput of 100 kg/h (max. 20 % dry biomass). The operating pressure is up to 35 MPa and the maximum reactor temperature 700 °C.

The feed system is qualified for the handling of different educts, such as solid biomass, mud (including sewage sludge) and liquid educts. A measured quantity of the feed is transferred into the stirred preparation tank (volume 1.5 m³) with a connected mill. The water content of the feed and the maximum size of the solid particles are adjusted to obtain a homogeneous feed, suited for pumping. The conditioned feed is transferred to the stirred store tank (volume 3 m³). The feed is dosed by a mass-flow controlled high pressure pump to the reaction system. Long time operation of the feed system sometimes causes trouble. It is expected that commercial plants with a flow rate 10 to 100 times higher will work 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 the compression of water up to 28 MPa consumes 1.6 kW.

The feed 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. The pre-heated feed 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 in 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 and to separate brines and solids. The reactor is constructed as down flow reactor. A feature of the VERENA plant is the brines removal via a third output from the lower part of the reactor. This helps to avoid clogging and to reduce fouling of the heat exchanger.

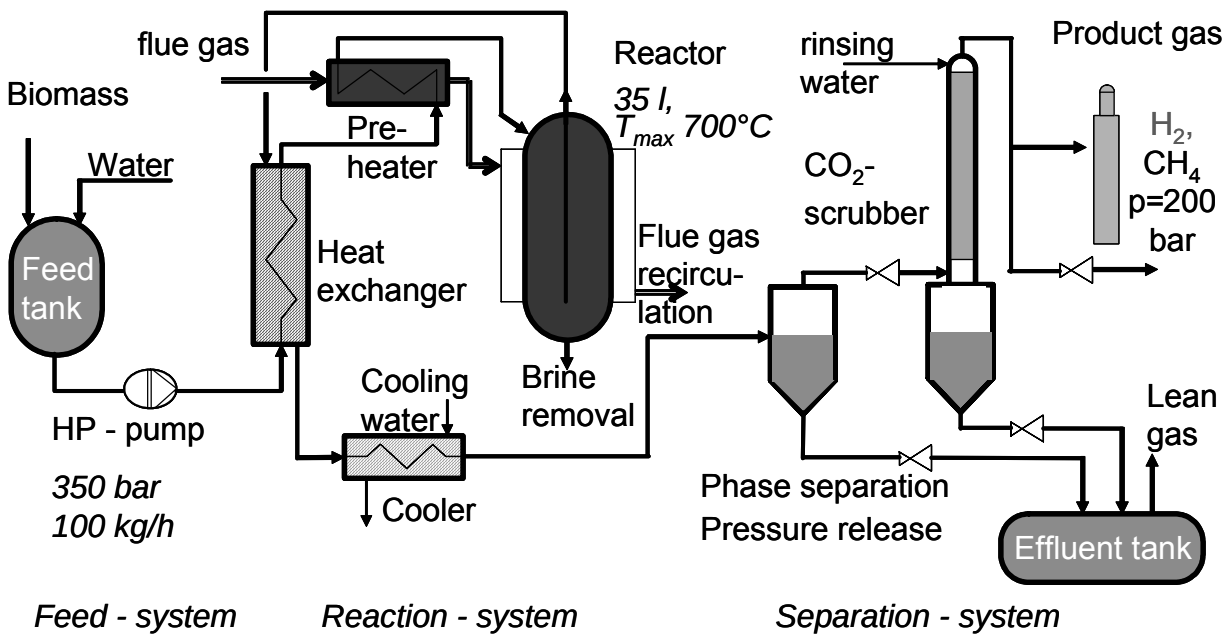

Figure 2: Simplified flow sheet of the pilot plant for the gasification of wet biomass in supercritical water "VERENA":

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 gases produced separate from the water phase. The two phases are separated and the pressure can be reduced in 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 (see Fig. 2). 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 will be filled into high pressure bottles. The excess of the produced gases are passed to a torch and will be burned.

Results and Discussion

Experiments in the laboratory scale apparatus with corn

Temperature is the most important parameter of the process. For corn starch as feed with a concentration of 5 wt % and at a residence time of 5 min the following observations have been done: The gasification yield will rise from 40 % at 550 °C to 95 % at 700 °C reaction temperature and 25 MPa pressure. Further experiments with the down flow reactor show that the gasification efficiency of corn silage in supercritical water can reach 100% (within the experimental error) at 700 °C reaction temperature. A temperature increase from 650 to 700 ° C improves the gas production by 20%. At lower reaction temperatures (300 °C) the gas production deteriorates, only less than 10% of the carbon is gasified. Antal et al. (2000) investigated the effect of the temperature on the gasification of corn starch in supercritical water with a carbon catalyst. They reported an increase in the carbon gasification efficiency from 0.91 at 690 °C to 1.06 at 805 °C reaction temperature.

Another important process parameter is the residence time. The yield curve in Figure 3 illustrates the influence of the residence time on the supercritical water gasification of corn silage. At a reaction temperature of 700°C, a linear relationship of the gas yield with the residence times has been measured.

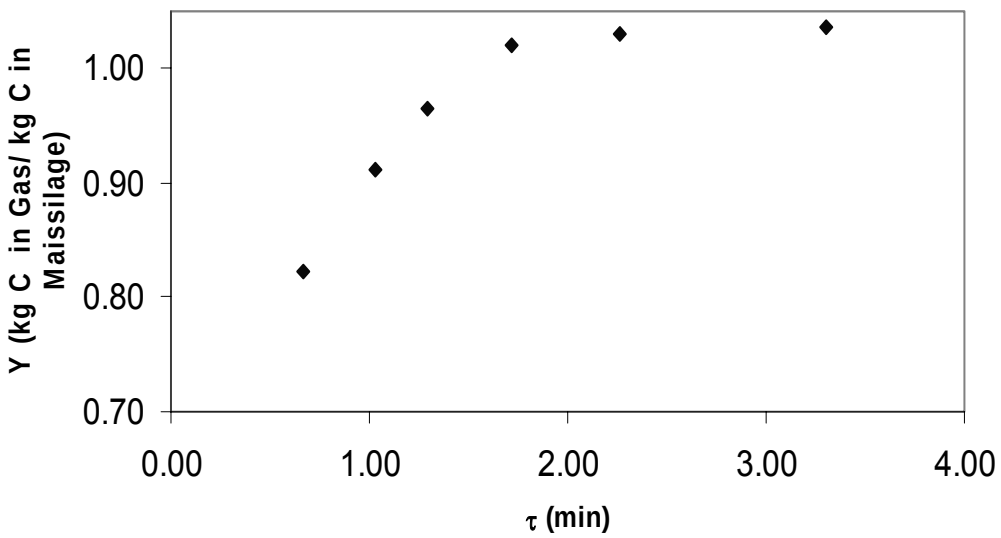

Figure 3: Gasification yield of corn silage as function of the residence time [corn silage] = 5 wt.-% T = 700 °C and p = 25 MPa

This effect of the residence time has also been observed for a reaction temperature of 650 °C. At lower reaction temperatures the gasification yield does not reach 100 % even at residence times as long as 6 min (longest residence times proved).

Experiments with the pilot plant VERENA

First task of this experimental program was the measurement of data for the energy flow in the different sections of the plant. To measure these process data, experiments with methanol solutions have been performed. Gasification of methanol proceeds without technical problems for a long time. The stable condition is a precondition to gain data for the energy balance. Biomass slurries with the same concentration are expected to give similar values (except the lower H_2 and the higher CH_4 concentrations of the product gas). The flow rate of the experiments with methanol solutions was between 90 and 100 kg/h. Residence time was about 1.9 min. The carbon balance could be closed within the accuracy of the measuring systems; the mean value is 99.9 ± 1.5. The composition of the product gas is illustrated in Figure 4.

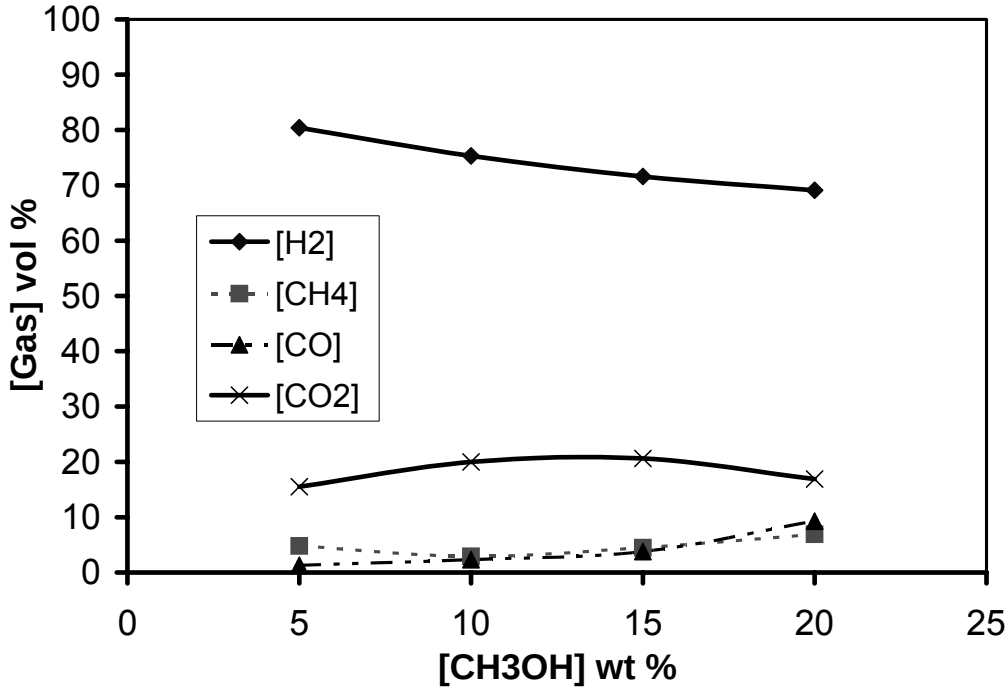

Figure 4: Gasification of methanol, product gas composition

Crucial for a high energy efficiency of the process is the function of the heat exchanger. More than 80 wt % of the feed mass is water, which has to be heated up to 600 °C and then cooled down to ambient temperature. One of the main reasons for operation under supercritical pressure is the possibility to apply conventional heat exchangers. Although the heat exchanger of the pilot plant VERENA is designed to enable several hardware configurations (flow sheets), only the most simple set up –one input and one output stream- will be described here. One of the challenges of the design of the heat exchanger was the lack of thermodynamic data of the multi component feed and product system.

The average reactor temperature (which was high enough for complete gasification) was 560 °C; the temperature of the product stream just in front of the heat exchanger (which is lower than the reactor temperature due to some heat losses) was 541 °C; the temperature of the product behind the heat exchanger (primary a heat loss which should be further used) was 159 °C. The feed temperature in front of the heat exchanger is 23 °C; the temperature just behind the heat exchanger was in all cases higher than the critical temperature of water (mean value 399 °C) for more details see (Boukis, 2004). During operation with water at supercritical conditions (flow rate 100 kg/h) a heat transfer coefficient k up to 700 $Wm^{-2}K^{-1}$ has been calculated.

During all experiments, the fuel (propane gas) consumption of the burner -for heating the reaction system- was somewhat less than 70 kW_{th}. Only 35 up to 43 kW_{th} from this amount

have been transferred to the reaction system. The energy input to the gasification process (see Fig. 5) is calculated by using only the heat consumption from the reaction system (without considering losses of the flue gas via chimney, all other heat losses have been considered). The energy of the educt methanol has been calculated as lower heating value of the amount of methanol used -before dilution with water- to form the feed solution. The electric power needed for the high-pressure pump and the other aggregates is only 2 kW_e.

Two calculations of the thermal efficiency of the system have been performed (LHV is for Lower Heating Value): First by the assumption of production of burning gas, lean gas and hot water. In this case the mean value is 86% (LHV of product gas + LHV of lean gas + warm water) / (Heat dissipation + electrical energy + LHV of pure methanol). Second by the assumption of production of only burning gas. In this case the mean value is 75%. The energy content of hot water has been calculated by the assumption of a residual temperature of the effluent stream of 40°C. The VERENA plant is a small facility with much higher heat losses per feed mass than future 10 times larger full scale plants. This has to be considered for the further evaluation of the experimental values. The heating system is not optimized for energy efficiency, but for low investment cost, heat losses via chimney are very high (about 50 % of the real heat demand of the reaction system at a temperature level of about 600 °C).

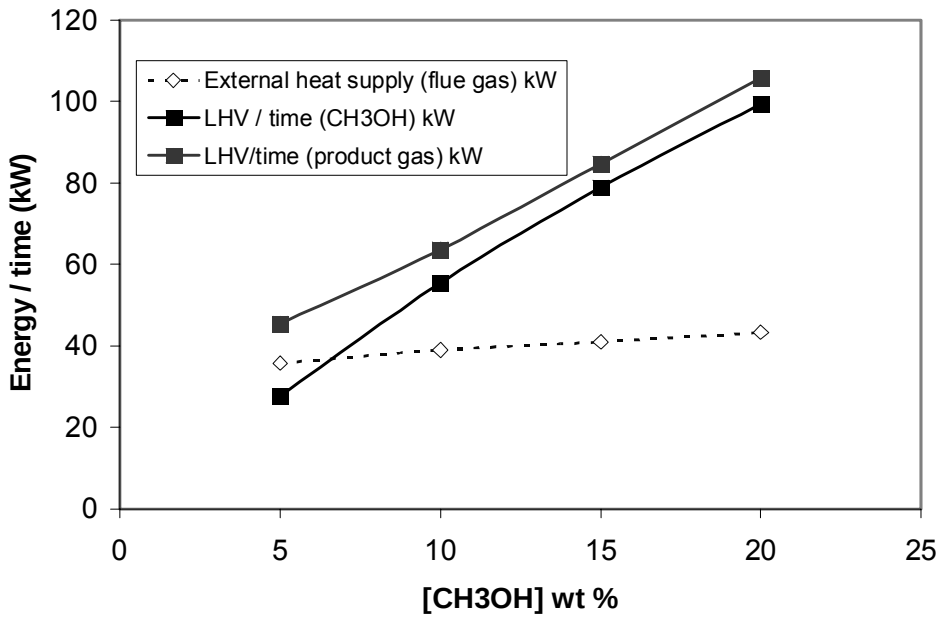

Figure 5: Energy / time consumption and production as function of the feed concentration.

One of the first experiments with biomass derived feeds has been performed with Pyroligneous acid. Pyroligneous acid is a by product of the vegetable charcoal production. This feed can be pumped without technical problems and has been used as feed for the hydrogen and methane production. Main constituent is an aqueous brownish-reddish colloidal solution with the typical smoke smell. The bottom, black colored sticky tar, has been separated before experiment and analysis.

Experimental conditions in the pilot plant VERENA were: Reactor temperature 620 °C, pressure 27 MPa, flow rate 50 kg/h, residence time 3.9 min. The duration of the experiment was 10 h (corresponding to 500 kg feed).

The conversion rate of carbon was high, 97 %. Main product was hydrogen (see Figure 6). The flow rate of the product gas was 4.48 Nm3/h. The carbon balance was closed with an accuracy of 98 %. Pyroligneous acid contains also phenols. At the experiment in the pilot plant VERENA the gasification yield of the of the phenols was lower that the overall carbon conversion (see Figure 7)

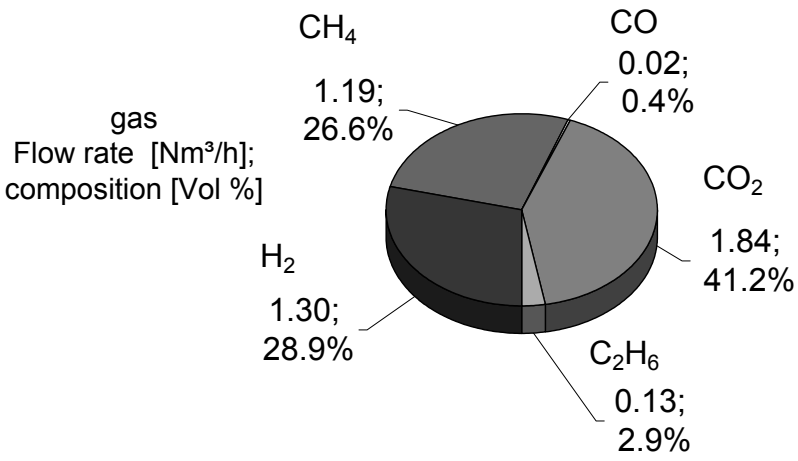

Figure 6: Product gas amount and composition from the gasification of pyroligneous acid in the pilot plant VERENA

The aqueous effluent had a yellow – orange color, naphthalene was detected. This diluted waste water has been qualified for the sewage disposal plant.

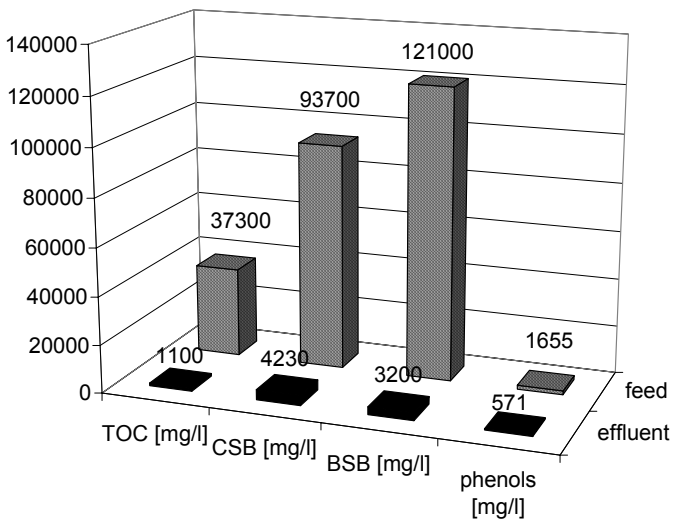

Figure 7: Compositions of the pyroligneous acid feed and the product solutions. (TIC: Total inorganic carbon, CSB: chemical oxygen demand)

Conclusion

The comparison with the traditional gasification process shows several advantages of the hydrothermal gasification, especially for wet biomass/organic waste feedstock. A gas rich in H_2 and methane can be produced from wet biomass in one process step. A high thermal efficiency of the process, including the heat exchanger, has been demonstrated and the soot and tar formation can be effectively suppressed.

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