Carbon dioxide removal in hydrothermal gasification of biomass

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The production of hydrogen and methane by reaction of organic matter using hydrothermal gasification is feasible for feedstock with high moisture content. Wastes from the agricultural sector can be used, e.g. grape residue, rests of plants or sewage sludge. Typical reaction conditions are temperatures of about 600 °C and a pressure of 30 MPa. By cooling, the product gas phase separates from the liquid effluent which will contain the inorganic compounds and a low quantity of residual organic matter.

A high pressure gas washer can be easily integrated in this gasification system resulting in a reduction of carbon dioxide content in the product gas and thus a higher hydrogen and methane partial pressure. This theoretical concept was demonstrated in the pilot plant VERENA.

Experimental data which will prove the effectiveness of this concept will be shown. Experiments for the carbon dioxide removal with a model gas mixture and during gasification experiments of real biomass were carried out. The model gas mixture used consisted of hydrogen (52 volume-%), methane (20 %), carbon dioxide (27 %) and carbon monoxide (1 %). This gas composition is similar to the gas phase achieved in many biomass gasification experiments. The gas flow, the water flow and the pressure in the washing column were varied in the experiments.

Up to 99 % of the carbon dioxide could be removed by this technique at optimized conditions. The hydrogen loss in the lean gas amounted to about 5 %, the methane loss to about 10 %. The cleaned model gas contained about 75 % of hydrogen.

Introduction

Hydrothermal gasification is a promising method to generate a product gas rich in hydrogen and methane. Educts with a high water content and thus low calorific value can be used without any pre-drying or upgrading step. At hydrothermal conditions the organic compounds react with water to form a fuel gas. Product gases like H_2, CO, CO_2 or CH_4 and many organic substances are soluble in supercritical water forming a one-phase system; transport limitation across phase boundaries will not occur (Boukis et al., 2002 and Boukis et al., 2004).

After cooling down, the water phase separates from the gas phase, which consists mainly of hydrogen and smaller amounts of methane, carbon dioxide, carbon monoxide and traces of other hydrocarbons like ethane, ethene or propane. According to our experimental results in the pilot plant VERENA, some of the carbon dioxide will be already dissolved in the aqueous effluent, but the most part is still present in the product gas. This carbon dioxide ‘dilutes’ the fuel gas and lowers its calorific value. The product gas is available at a pressure level of about 20 MPa.

Numerous data are available for binary mixtures at high pressures of water and the main components carbon dioxide, hydrogen and methane, e.g. Wiebe (1941), Stephen (1963), Young (1981), Battino (1982), Dohrn et al. (1986), Clever et Al. (1987), Dohrn et al. (1987), Abdulagatov et al. (1993), Scalise at al. (1994), Chapoy et al. (2003), Diamond et al. (2003), Spycher et al. (2003), Chapoy et al. (2004a), Chapoy et al. (2004b), Li et al. (2004), Valtz et al. (2004). Experimental data for multi-component mixtures are rare. Kremer (1989) tried to develop a correlation equation for the solubility of the pure gaseous components and the multi-component mixtures. He reported relative errors of up to 15 % for pure gases and 28.8

% for multi-component mixtures compared to available experimental data, what he ascribed to experimental data scattering.

The main consequence of the available data is that the solubility of carbon dioxide in water in the interesting pressure (<25 MPa) and temperature (15 – 25° C) range is much better than the solubility of the other fuel gas compounds. This permits the implementation of a simple and effective carbon dioxide removal by absorption with pure water at ambient temperature without addition of base materials like amines.

A high pressure gas washer can be easily integrated in the system resulting in a reduced carbon dioxide content in the product gas and a higher hydrogen and methane partial pressure.

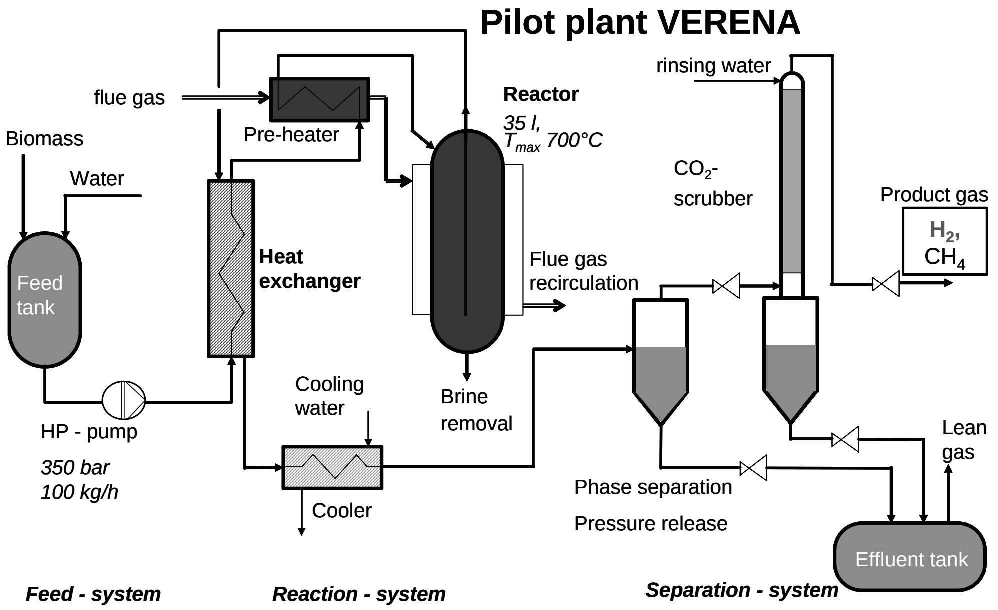


Figure 1: flow sheet of the pilot plant VERENA.

First experiments on carbon dioxide removal were carried out during gasification tests in the pilot plant. The gas flow was low (about 0.2 m^3/h at standard conditions) in these experiments. The hydrogen content in the product gas amounted to 84.6 volume-% before the CO_2-scrubber. After removal of about 99 % of the carbon dioxide, the cleaned gas consisted of 94.7 volume-% of hydrogen and small quantities of carbon dioxide, carbon monoxide and hydrocarbons (see figure 2). The lean gas of the scrubber contained about 95 % of carbon dioxide and 5 % of hydrogen.

A series of experiments was planned for a systematic study of the carbon dioxide removal. A gas mixture filled in gas cylinders was used to get a constant gas composition and adjustable gas flows for constant operation of the carbon dioxide scrubber. This enabled the operation of the carbon dioxide scrubber without the need to run the whole plant VERENA.

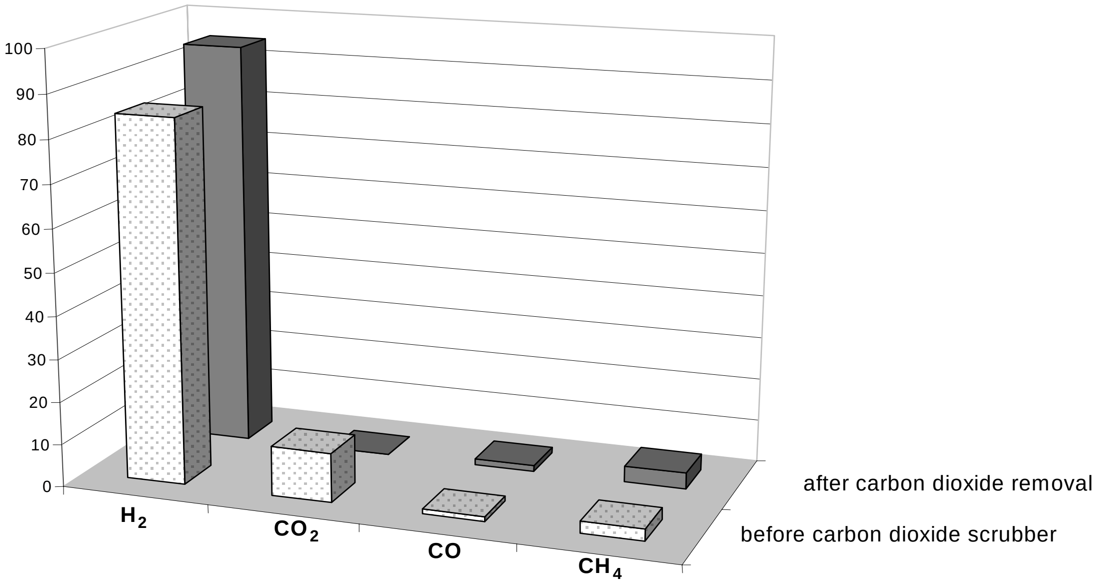


Figure 2: Gas composition during the first test of the carbon dioxide scrubber in the pilot plant VERENA. Gas flow 0.2 m³/h at standard conditions, 20 l/h of rinsing water at 20° C at p=10 MPa in the scrubber.

Experimental

The experiments were performed in the pilot plant VERENA. Only the carbon dioxide scrubber, the pressure regulation system, the gas analysis system and the torch were applied.

A gas mixture with 52 volume-% hydrogen, 27 volume-% carbon dioxide, 20 volume-% methane and 1 volume-% carbon monoxide was used. This gas composition was similar to the product gas we got in many gasification experiments. The gas was supplied by Messer Griesheim in gas cylinders at a pressure of 13 MPa. The gas flow was adjusted using a Bronkhorst Hi-Tec mass flow controller which was connected to the gas cylinders and the carbon dioxide scrubber. Due to technical requests of the mass flow controller, the pressure in the carbon dioxide scrubber was limited to 10 MPa.

The rinsing water for the carbon dioxide scrubber was fed by a LEWA high pressure pump with a maximum capacity of 50 l/h. The temperature of the water was about 21° C (ambient temperature) in the experiments. The carbon dioxide scrubber was a high pressure steel tube with a length of about 2.2 m and an inner diameter of 5 cm. The column packing consisted of a wire fabric.

The gas composition was measured in-line with an ABB Advance Optima detector for H_2, CH_4, CO_2 and CO and off-line by gas chromatography. The gas flow was taken by a rotary piston gas meter (Aerzen) for the cleaned gas and a Ritter gas meter for the lean gas.

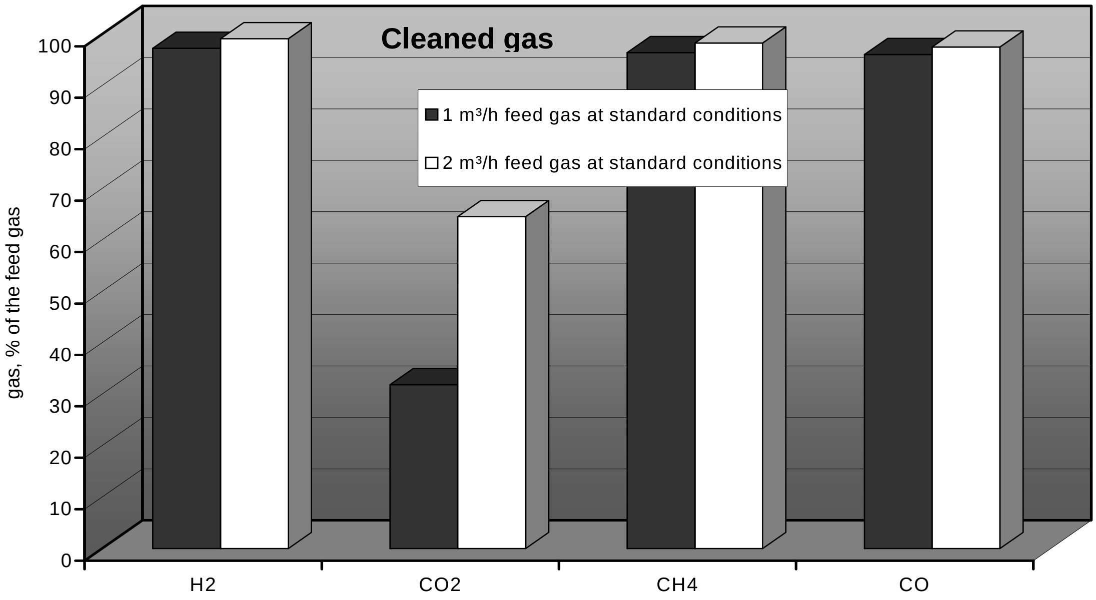
Results and discussion

The gas flow, the amount of the rinsing water and the pressure inside the carbon dioxide scrubber were varied in the experiments. The experimental conditions are listed in table 1.

At a pressure of 5 MPa inside the scrubber, about 68 % of the CO_2 in the feed gas could be removed for a feed gas flow of 1 m³/h at standard conditions. Increasing the feed gas flow to 2.1 m³/h reduces the amount of removed carbon dioxide to 35 %. Most of the removed carbon dioxide will be found in the lean gas after expansion of the rinsing water, a small amount will still be dissolved at ambient conditions, the carbon dioxide balance was closed to 100%. Hydrogen loss via rinsing water is in the range of 2.5 % (for 2.1 m³/h of feed gas flow) and 1 % for 1 m³/h feed gas flow.

Table 1: Experimental conditions.

Test No.	Gas flow at standard conditions, m³/h	Rinsing water, l/h	Pressure, MPa
1	2.1	15	10
2	2.1	25	10
3	3	40	10
4	2.1	25	7.5
5	2.1	25	5
6	2.1	25	7.5
7	2.1	25	7.5
8	1	25	5



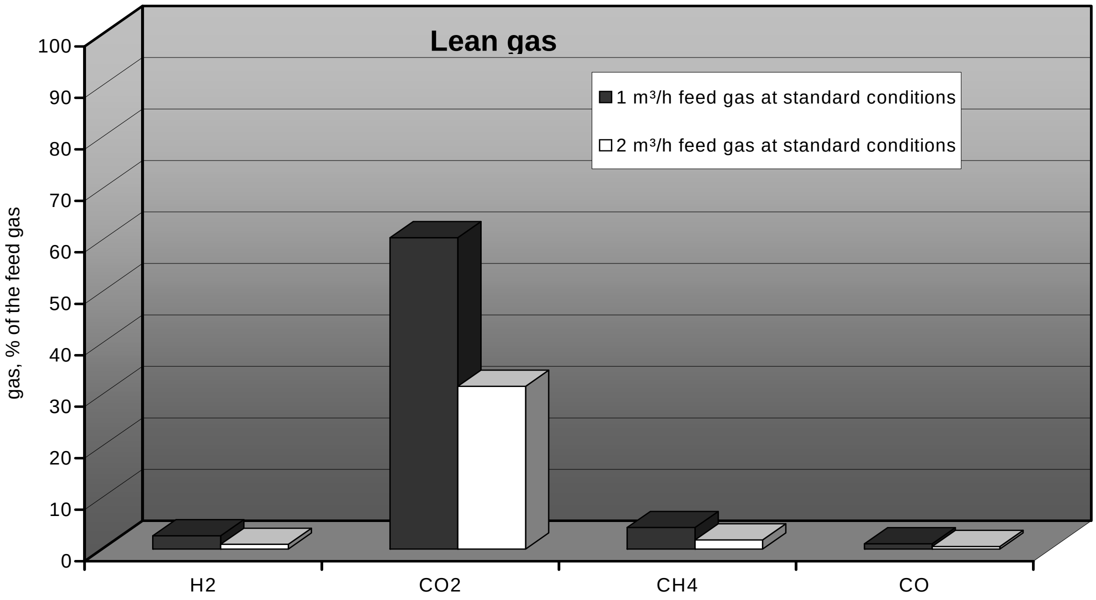


Figure 3: Relative amount of cleaned gas compounds (top) and lean gas compounds (bottom) at p=5 MPa in the carbon dioxide scrubber, 25 l/h of rinsing water and feed gas flows of 1 and 2.1 m³/h at standard conditions.

Much CO_2 will be removed from the feed gas if the pressure inside the carbon dioxide scrubber is increased (figure 4). At 5 and 7.5 MPa, a considerable amount of carbon dioxide is still present in the cleaned gas. Increasing the pressure to 10 MPa significantly improves the carbon dioxide removal. Only 1 % of the initial carbon dioxide amount is detected in the cleaned gas. At the same time, the losses of hydrogen and methane will rise up to 5 % (hydrogen) and 10 % (methane) compared to the initial values in the feed gas.

Since the solubility of carbon dioxide will increase almost linearly with pressure, improved mass transfer inside the column may cause this strong drop in carbon dioxide fraction. If the pressure is increased at constant mass flow of the gas, the real volume flow decreases at the same time. The improved mass transfer causes the simultaneous loss of hydrogen and methane by absorption.

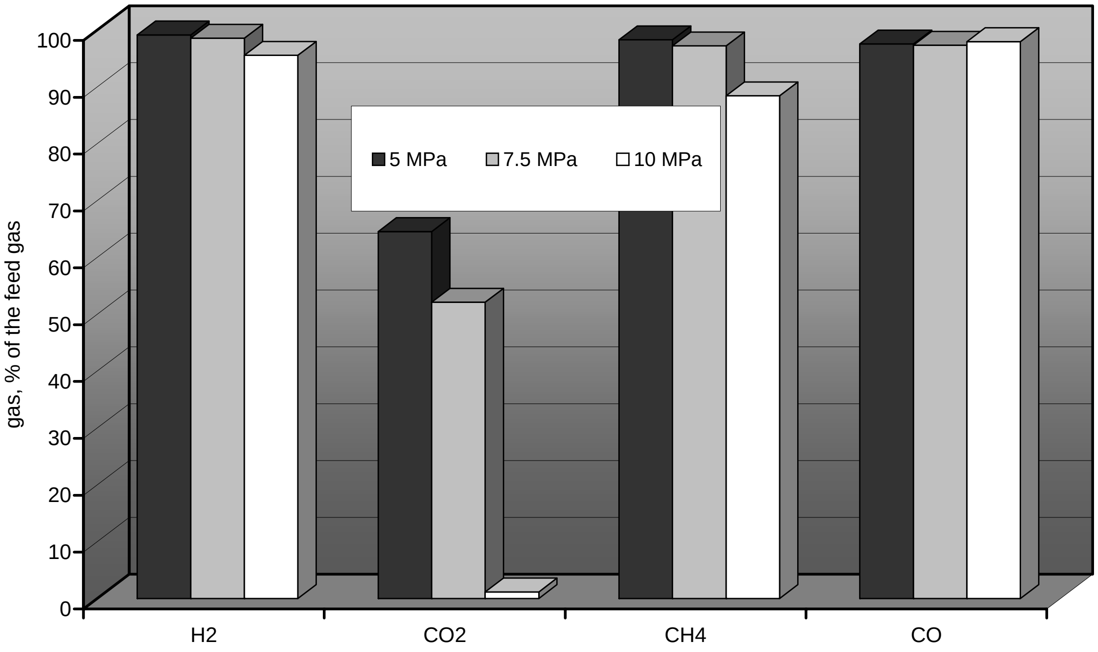


Figure 4: Composition of the cleaned gas at p = 5, 7.5 and 10 MPa in the carbon dioxide scrubber, 25 l/h of rinsing water and a feed gas flow of 2.1 m³/h at standard conditions.

The influence of column throughput at a constant ratio of rinsing water and feed gas for a pressure of 10 MPa is shown in figure 5. The rinsing water flow was adjusted to 25 l/h for the feed gas flow of 2.1 m³/h, for a feed gas flow of 3.5 m³/h at standard conditions the water flow was raised to 40 l/h, so that the ratio of the flows of rinsing water and gas will be kept constant.

When the gas throughput was increased from 2.1 to 3.5 m³/h, only a slight effect in the range of 1 to 2 % on the amounts of hydrogen, methane and carbon monoxide in the cleaned gas is detectable. A clear effect can be seen for the carbon dioxide amount. The absorbed amount of CO_2 is reduced from 99 % to about 90 % relating to the amounts in the feed gas.

At a constant ratio of feed gas to rinsing water, thermodynamics predicts that the same percentage of carbon dioxide will be soluble in the water at equilibrium. Reduced mass transfer due to the higher flow velocity and thus shorter contact time in the column causes the drop in solubility.

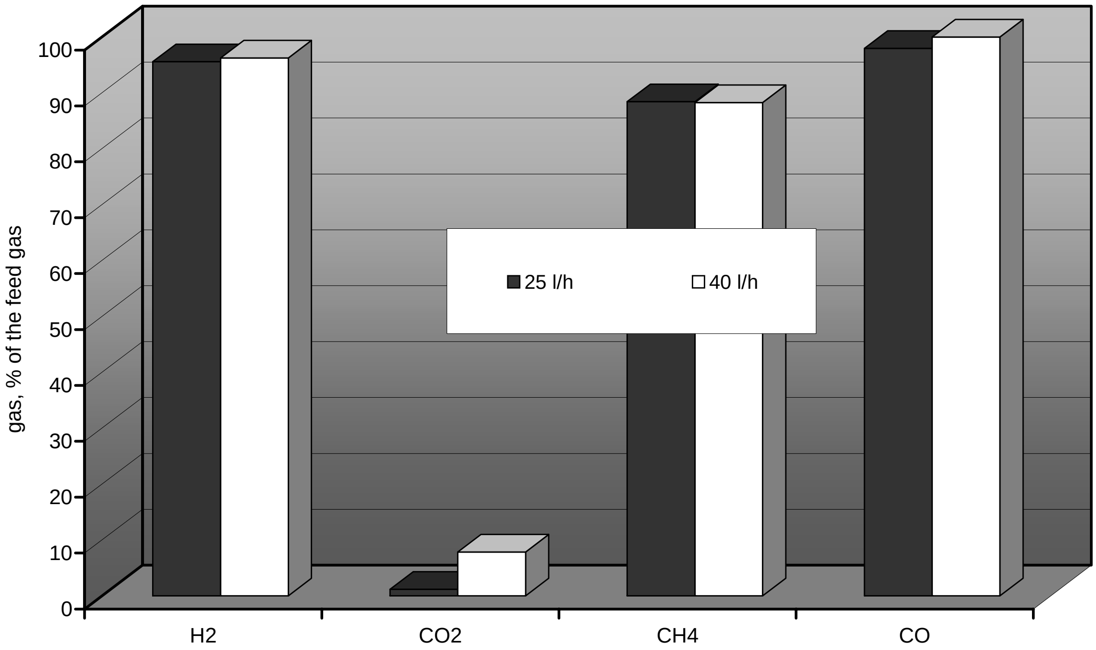


Figure 5: Relative amount of cleaned gas components at p = 10 MPa in the carbon dioxide scrubber, 25 l/h of rinsing water (feed gas flow of 2.1 m³/h at standard conditions) and 40 l/h of rinsing water (feed gas flow of 3.5 m³/h at standard conditions).

Conclusions

The feasibility of the theoretical concept of carbon dioxide removal by high-pressure absorption with pure water was demonstrated. Almost complete removal of CO_2 is possible. The losses of hydrogen and methane are low; the lean gas may be used for additional reactor heating.

Further analysis of the experimental data and detailed modelling will be needed to get optimized conditions for the carbon dioxide separation. Some experiments at higher pressure (about 20 MPa) that could not be carried out with the existing setup should be performed during gasification experiments in the pilot plant VERENA in the near future. This will complete the database.

The modelling using the experimental database will solve the optimization problem of maximum CO_2 removal at minimal H_2 and CH_4 loss.

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