Biomass gasification in supercritical water

Boukis, Nikolaos; Diem, Volker; Dinjus, Eckhard; Gall, Ulrich; Kruse, Andrea
Institute for Technical Chemistry, Forschungszentrum Karlsruhe
P.O. Box 3640, D-76021 Karlsruhe, Germany;
Tel: +49 7247 82 4825, fax: +49 7247 82 2244, e-mail: nikolaos.boukis@itc-cpv.fzk.de

ABSTRACT: Gasification of biomass with a high water content (about 80 wt. %) in supercritical water has several advantages compared with combustion or gasification at ambient pressures. At temperatures and pressures above the critical point of water (T=374°C, p=22.1 MPa), the reaction of the organic substances with water proceeds fast and completely with high space-time yields. Desired product is an hydrogen rich fuel gas. Carbon forms preferentially CO2, methane is a byproduct. The CO2 can be easily separated from the product gas, and stored under pressure. Until now, most of the investigations have been performed in laboratory scale equipment with model compounds in continuous flow tubular reactors and real material in batch experiments. At temperatures of 600°C and about 25 MPa a complete gasification can be achieved. The presence of potassium is important for a high hydrogen yield. Low CO yield in the product gas as well as low tar and char formation are further advantages of the process. Based on the encouraging experimental experiences with laboratory scale equipment and with an 10 kg/h continuous flow plant operated for a similar process, a new continuous flow plant dedicated for the process of biomass gasification in supercritical water has been installed and is now put in operation.

Keywords: hydrogen, agricultural residues, organic waste

1 INTRODUCTION

Using biomass for energy generation offers the potential to reduce the rise in atmospheric CO2 concentration and supports national and European efforts in climate protection.

A lot of the residual biomass appears as wet material containing up to 95 wt. % of water. Wet residual biomass amounts to some 107 Mg/a (DOM) corresponding to an energy content (heating value) of several hundreds PJ/a in Germany. More data concerning the amounts of residual biomass can be found in other presentations of this conference.

Traditional gasification achieves low efficiencies at these high water contents (in the order of 10% cold gas efficiency at 80% water content). Under high (supercritical) pressure, heat exchange is effective. Estimations on the basis of thermodynamic data give an about six times higher gas efficiency for gasification in supercritical water at a temperature of 600°C and a pressure of 30 MPa. The density of water is approximately one order of magnitude higher than the density of water vapor at 250°C and 1 MPa. This gives rise to an increased space-time yield. Higher thermal conductivity and higher temperature have a positive impact on the endothermal reforming reaction, generally accelerating it. Supercritical water forms a one-phase system with the main product gases H2, CO, CO2, CH4.

Concerning process technology, there is a simple possibility of producing hydrogen at high pressures as required for storage in pressurized tanks. In addition, a cost and energy effective scrubbing step for CO2 removal under pressure can be integrated. This treatment increases the hydrogen partial pressure. If an applicable long-term storage for the water – CO2 mixture under pressure is available, and then the process offers a new method to avoid completely CO2 emissions.

First experiments to convert carbohydrates to liquid products in supercritical water were performed by Modell and Amin in the mid 1970s at MIT [1]. Systematic experimental investigations for the conversion and gasification of biomass, for waste model compounds and for real wastewater under hydrothermal conditions were carried out at the Pacific Northwest Laboratories (PNL), at the university of Hawaii and at the National Institutes for the Resources and Environment [2], Japan (NIRE).

In the research center Karlsruhe numerous experiments with model substances and limited experiments with real biomasses were performed in supercritical water in continuous facilities of various capacities, [3-5]. High pressure experiments in a continuous flow reactor with real biomass slurry represent a special experimental challenge at low rates.

At present, a pilot plant with a throughput of 100 kg/h of aqueous biomass (educt) has been installed and is now put in operation. The new facility, VERENA (a German acronym standing for "experimental facility for the energetic exploitation of agricultural matter"), should be expanded into a complete energy generation system on a medium term.

2 EXPERIMENTAL

2.1 Process description

If necessary, the educt is subjected to a preliminary treatment. Depending on the quality of the educt, this treatment takes place in a separator for the separation of inorganic solid impurities and the decanting of accompanying water or in a mixing tank for educts of variable origin. Furthermore catalytical effective additives are added to the educt, if required. Then, the conditioned educt is passed on to the high-pressure feed system. Depending on the quality of the educt, this system is of variable design. Preliminary crushing is required for solid-containing educts in order to ensure a reliable operation of the high-pressure dosage pump. The operating pressure is typically about 30 MPa.

The educt flow is heated to the required temperature for the gasification reaction (500 – 700 °C) (e.g. C6H12O6 + 6 H2O → 12 H2 + 6 CO2; ΔH = 158.7 kJ/mol, 882 kJ/kg) and the sensible heat (e.g. H (400 – 600°C) = 1292 kJ/kg. The volume of the reactor is large enough to enable a residence time of at least 1 min.

The effluents are passed on to a separation system, where the product gas is expanded to the pressure required for further treatment. This energy might be
recovered by an expansion turbine. Via a level control, the water phase leaves the separator. Depending on the educt quality, the water phase may contain solids that have to be removed in an additional separator. Part of the effluents can be recycled. Qualification of the effluents and solids with regard to management and disposal is an important topic. The objective is to reach the limits specified for direct discharge via sewers.

2.2 Educts and Apparatus
The model compounds glucose for cellulose, catechol and vanillin for lignin and glycine for proteins were used as aqueous solutions. Real biomass (vegetable foodstuff and vegetable wastes) was treated in batch autoclaves and recently in continuous flow reactors. Experiments with solids have been performed by the addition of a certain amount of the material to the autoclaves. Continuous flow experiments in small apparatuses have been performed by pumping fresh water to the preloaded 20 ml autoclave to entrain product gas continuously and regulate pressure to the desired level.

Experiments with methanol instead of biomass were performed to demonstrate the long time stability of the gasification reaction in supercritical water [6].

For a detailed description of the laboratory equipment used see also [3, 6]. The pilot-plant VERENA is described separately in chapter 4.

3 RESULTS AND DISCUSSION
3.1 Methanol
The conversion of methanol in or with supercritical water under the experimental conditions (p=25 MPa, T_max=600 °C, flow rate about 1 ml/min) resulted in a product gas rich in hydrogen. Carbon is converted to a mixture of CO_2, CO and CH_4. In all experiments performed, the conversion rate was higher than 98 %, see Fig. 1. Although no catalyst has been used in these experiments, there is evidence that the inner surface of the reactor influences the composition of the product gas. This phenomenon is not clear yet and further work is under progress to clarify this effect.

![Figure 1: Gas composition and conversion rate as function of the methanol concentration.](image)

The apparatus was continuously operated for several weeks. Operation with 5 wt.% methanol lasted over 1000h. The operation, concerning gas production and quality, was stable. After the experiment the reactor has been inspected for residuals. Soot formation was negligible. The overall operating life of the plant in the meantime has reached approximately 3000 h without any major disruptions. All the samples of the product solution were clear, odorless and chemical analysis showed only negligible traces of compounds higher than C1. Remarkable is the high amount of hydrogen in the product gas. The gas composition and especially carbon monoxide and the carbon dioxide concentration is strongly influenced by the methanol concentration of the feed mixture (see Fig. 1).

3.2 Model compounds
It is known that cellulose hydrolysis proceeds very fast [7], therefore it is better to use glucose instead of cellulose. Glucose can be fed to the reactor as an aqueous solution. Some few mmol of potassium salts have been added to the feed to increase gasification efficiency and to lower CO content; see also [4].

At low temperatures some (in the order of few wt %) soot and tar is formed. At temperatures higher than 550°C complete gasification of glucose occurs. Formation of solid and oily by-products can be suppressed down to trace level. The aqueous effluent (residual TOC) contained mainly phenol and phenol derivatives. Obviously phenol compounds, which are supposed to be less reactive than glucose are formed from glucose.

![Figure 2: Simplified reaction scheme of cellulose decomposition in near- or supercritical water.](image)

The main reaction paths for glucose are known [8 - 10] and represented in Fig. 2 in a simplified manner. It is expected that a rapid hydrolysis of cellulose to sugar units, e.g. glucose and fructose, first takes place. This hydrolytic depolymerization is followed by decomposition reactions to short-chain aldehydes and acids compete with dehydration and ring closure to furfural derivatives or phenols. The short-chain aldehydes and acids react to the gaseous products desired. The phenols and other aromatic compounds generated are also decomposed to gases under the conditions of biomass gasification in supercritical water. On the other hand, undesired tar, soot or coke may be produced from these aromatic compounds.

The next step was to study the consequences of the formation of aromatic compounds by the degradation of the aromatic compound, pyrocatechol. Pyrocatechol is also a model substance for lignin. Again KOH was added in the aqueous pyrocatechol feed solution.

Calculations with the computer program equiTherm show an evident temperature dependence of the gas phase
composition. The calculated equilibrium value of the relative hydrogen yield (see Fig. 3) is nearly reached after two minutes reaction time at 600°C. The hydrogen yield decreases with pressure.

Figure 3: Calculated equilibrium and measured hydrogen yield at 600°C and 20, 30, 40 MPa (concentrations 0.6 mol/l pyrocatechol and 0.005 mol/l KOH).

The calculated equilibrium value of methane formation (see Fig. 4), which is increasing with pressure is not attained after 4 min. reaction time at 600°C. The reason for this might be that methane formation and methane decomposition are kinetically inhibited reactions at the experimental conditions. Higher hydrocarbons with up to four carbon atoms are formed with a yield of up to 0.6 mole/mole pyrocatechol. Their contents decrease with pressure and reaction time.

Figure 4: Calculated equilibrium and measured methane yield at 600°C and 20, 30, 40 MPa (concentrations 0.6 mol/l pyrocatechol and 0.005 mol/l KOH).

The residual TOC content decreases evidently with reaction time and slightly with pressure. At 600°C and an initial concentration of 0.6 molar pyrocatechol the TOC of the product solution decreases to less than 0.3% after 2 min reaction time independent of the pressure. The residual TOC content, if there was enough material to analyze, consisted mainly of phenol and small amounts of methyl-, ethyl- and propylphenols, as well as naphthols and indanone. The carbon deposit as solid residue (elementary carbon and organic carbon) after experiment is between 1.7-5.2% of the carbon of the input flow at 20 MPa pressure (subcritical). It decreases at 30 MPa or higher process pressure to less than 0.4%. The solid residue contains also potassium and other metals dissolved from the metal walls of the reactor. This means that even the aromatic compounds react with supercritical water to form gases, see also [4].

3.3 Waste biomass

Waste vegetable biomass (only 260 mg) was dried, crushed and filled into the autoclave. Water (1 ml/min) was continuously pumped at 25 MPa. Reaction temperature was 500–700°C and the reaction time was 25 minutes.

Several experiments conducted indicate carbon conversion up to more than 95%; the main constituents of the product gas are hydrogen (> 70 vol.%), carbon dioxide and methane, while higher alkanes and carbon monoxide were found only at lower concentrations. The carbon-like residue was always below 3%. Fig. 5 shows the gas composition after the gasification of biomass at 600°C.

Figure 5: Gas composition for gasification of vegetable waste biomass in supercritical water (feed: 260 mg of dried waste biomass, p = 25 MPa, T = 600°C, reaction time = 25 min, carbon-like residue < 5%).

The dependence of the amount of the gas formed from the reaction temperature show a strong influence of temperature (see Figure 5). The temperature of 700 °C represents a limit for a technical application due to the properties of available reactor materials.

Figure 6: Gas production as function of the reaction temperature (for the other experimental data see Fig. 5)

4 THE PILOT-PLANT VERENA

Based on the experimental results in laboratory scale a pilot plant (VERENA, see Fig. 7), with a total throughput of 100 kg per hour (max. 20 % dry biomass) was planned and is still under construction and first test operation. The plant is designed for an operating pressure
of up to 35 MPa and a maximum temperature of 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 educt 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 solid particles are adjusted to obtain a homogenous feed suited for pumping. The conditioned educt is transferred to the stirred store tank (volume 3 m³) which has a capacity for 30 hours of continuous operation. The feed is dosed by a mass-flow controlled high pressure metering pump to the reaction system. The feed system was tested successfully with more than one ton of raw waste biomass.

**Figure 7: VERENA - simplified process flow-sheet.**

The educt flow passes a double-pipe heat exchanger and is heated in countercurrent flow by the hot effluent from the reactor (=600°C). The pre-heated educt is lead into the reactor, which is heated by externally generated flue gas. It has a total volume of 40 dm³, can be operated up to 700 °C and is divided into two parts. The first part is a tubular reactor which acts primarily as heat exchanger, the second part is a slim vessel to guarantee the required residence time of at least 1 min. 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 were separated and the pressure can be reduced alternatively in one or two steps. One separator is equipped with an integrated CO2 scrubber. Here, the CO2 content in the product gas is reduced by the addition of cold water for increasing the solution capacity for CO2. The amount of cold water added serves to control the reduction of the CO2 content and the fraction of burnable gases (H2, CH4, CO) of the product gas in the water phase of the scrubber. 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 eventual solids from the effluent. Then the effluent is lead to a store tank.

The burnable gases can be used principally in different ways for energy generation or chemical reactions. In the VERENA plant the use of product gases is not provided in the first stage. They are passed to a torch and will be burned.

**5 CONCLUSIONS**

The process of hydrothermal biomass gasification has been studied in numerous laboratory-scale experiments. The comparison to the traditional gasification process shows some advantages for the hydrothermal gasification especially for wet biomass/organic waste feedstock:
- a much higher thermal efficiency is expected,
- a H2 rich gas can be produced in one process step,
- soot and tar formation can be suppressed, and
- the heteroatoms (S, N, and halogens) leave the process with the aqueous effluent. An expensive gas cleaning is not necessary.

In further experiments, the optimization of the process parameters is focused to the increase of the feed concentration to more than 10 wt% organics (DOM). In addition, the influence of the type and concentration of the starting material on the composition of the product gas will be investigated further. Technical aspects of the process, such as heat exchanger efficiency, fouling, corrosion, thermal efficiency, solids discharge, and long-term availability, will be studied in the new pilot plant VERENA.

**6 REFERENCES**