Gasification of biomass in supercritical water (SCW)

A. Möbius*,1, N. Boukis1 and J. Sauer1

1 Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Conversion of wet biomass via gasification in supercritical water is a promising technology for the production of hydrogen and methane from renewable resources. The properties of water above the critical point enable reactions for the fast degradation of biomass and generation of a product gas consisting of hydrogen, methane, higher hydrocarbons and carbon dioxide without disturbing sulphur- and nitrogen-containing gases. In this article an overview over the supercritical water gasification will be given, which contains different types of laboratory-scale apparatuses as well as pilot plant scale and model substances as well as real biomasses.

Keywords: supercritical water; hydrothermal biomass gasification; hydrogen

1. Introduction

Due to declining reserves of fossil energy sources as coal, oil and gas, and the rising concentration of CO2 in the atmosphere the search for alternative fuels is one of the main foci of current research. Renewable energy can be obtained from biomass conversion or natural resources as sunlight, wind, tides, waves and geothermal heat. The beneficial use of biomass is the wide product range. Besides fuels also raw material for the chemical industry can be obtained directly.

Several methods for biomass conversion are already in use. Vegetable oil for example is used for biodiesel production via transesterification, ethanol is recovered from sugar and starch via hydrolysis and fermentation, and methane is obtained via anaerobic digestion of manure and maize. The best known application of biomass is the combustion of wood.

Especially the utilisation of wet biomass without drying offers a great potential as biomass itself and waste streams of agriculture and food production are available with a high water content. The production of gaseous fuels allows the use in already existing systems like turbines and motors as well as systems under research like fuel cells. Via syntheses like Fischer-Tropsch liquid biofuels can be produced.

Hydrothermal gasification combines these two aspects and offers the additional advantage of nearly complete conversion to hydrogen, methane and carbon dioxide at relatively low temperatures of 600-700°C. The carbon monoxide content of the product gas is very low. The produced carbon dioxide can be easily separated because of its high solubility in water under pressure. No drying of the biomass is necessary and not a gas, but a liquid has to be pressurised for the process, which saves costs.

2. Supercritical water

Water is a non-toxic, safe abundant and cheap solvent for many biochemical and chemical reactions. At ambient conditions of temperature and pressure, it exists as a liquid phase. Increasing the temperature or decreasing the pressure and passing the vapour pressure line it turns into a gaseous phase. Above the critical point (Tc=374°C, pc=22.1MPa) water and steam are indistinguishable, they are a single phase called “supercritical fluid”. The properties of this supercritical fluid are fluctuating between liquid and gas depending on the property and the conditions of temperature and pressure.

The density of supercritical water (SCW) ranges between the values of gaseous water and liquid water and can be varied over a wide range, see fig. 1. The viscosity of SCW is in the range of superheated vapour and therefore much lower than the one of liquid water. These two properties enable high reaction rates because of low mass transfer limitations.

The low values of the dielectric constant of about 5 to 15 [1] above the critical point compared to 78,5 at ambient conditions enable a high miscibility with many organic compounds and gases, on the other hand supercritical water is a poor solvent for ionic species like inorganic salts.
3. Supercritical water gasification

3.1 Supercritical water gasification of model substances

Glucose serves as a model substance, because it mimics the composition of the carbohydrates contained in biomass. Decomposition of glucose in supercritical water follows this reaction:

\[
C_6H_{12}O_6 + 6 H_2O \rightarrow 6 CO_2 + 12 H_2 \tag{1}
\]

Yu et al. found, that Glucose at low concentrations (0.1 M) can be completely gasified after 34 s at 600°C and 34.5 MPa [3]. Besides hydrogen and carbon dioxide, methane and carbon monoxide, also trace amounts of ethane and ethene were produced. At higher concentrations of glucose the gas yields are decreasing except for carbon monoxide. For SCWG of 0.1 M glucose at 600°C, 34.5 MPa and 34 s reaction time in a reactor made of Inconel a total gas yield of 14 mol/mol was reached. No char or tar products were detected.

Another main component of biomass is cellulose. After hydrolysis in supercritical water glucose is formed. Resende et al. studied the influence of temperature, concentration and reaction time [4, 5]. They used quartz capillary tubes as mini-batch reactors to avoid influence of the reactor material on the reaction. The longer the reaction proceeds less carbon dioxide and carbon monoxide is produced. On the other hand the share of hydrogen and methane increases. With increasing temperature the yield of all gases is increasing, but the composition of the product gas is changing. As for a longer reaction time the share of hydrogen and methane is increasing and the share of carbon monoxide and carbon dioxide is decreasing. The cellulose loading is an important cost factor as higher concentrations of biomass will reduce the capital and operating costs for the process. Both the composition of the product gas as the gas yields are affected by increasing cellulose concentration. Methane is the major product at low cellulose concentrations, but with increasing cellulose concentrations the mole fraction of methane is declining and the mole fractions of carbon monoxide and hydrogen increases. For SCWG of 9 wt. % cellulose at 600°C, a water density of 0.08 g/cm³ and 5 minutes reaction time a total gas yield of 15 mmol/g was reached. At the internal walls of the quartz reactors low amounts of char were found.

A further main component of biomass is lignin. It is a natural organic polymer with an irregular structure, which is thermoplastic and completely insoluble in solvents [6]. Resende et al. found comparable influence of temperature, reaction time and concentration on the gas yields for cellulose and lignin [5, 7]. Only the hydrogen yield decreases with increasing lignin loading, while it increases with increasing cellulose loading. The total gas yield was lower than for cellulose. For SCWG of 9 wt. % lignin at 600°C, a water density of 0.08 g/cm³ and 45 minutes reaction time a total gas yield of 11 mmol/g was reached. Also low amounts of char at the internal walls of the quartz reactors were found. Weiss-Hortala used phenol as an intermediate of lignin hydrolysis [8]. They found the same influence on the total gas yield and the hydrogen yield during the gasification of glucose.
DiLeo et al. used glycine as model substance for animal derived material [9]. Temperature seems to have a lower influence on gasification efficiency as they found in the aqueous phase almost the same amount of residual carbon at 500 and 600°C. The gas yields also did not change much with increasing reaction time. For SCWG of 10 wt. % glycine at 500°C, a water density of 0.079g/cm³ and 60 minutes reaction time a total gas yield of 0.25 mol gas/mol glycine was reached. In the quartz reactors a solid, black residue was found.

### 3.2 Supercritical water gasification of real biomass

In the last years more and more experiments with real biomasses were conducted. Besides agricultural products like corn and grass [10, 11] also industrial residues like sewage sludge [12] and pyroligneous acid [13] and increasingly algae [14-18] are subject of interest.

Kruse et al. studied the influence of different types of proteins on the gasification and found in general low gas yields for protein containing biomass, but differences between biomasses originating from plants and those containing meat. Animal biomass produces much smaller relative gas yields than vegetable biomass [19].

Depending on the composition of the feed (share of carbohydrates, lignin, proteins, water) the gasification efficiency for these biomasses is different. D’Jesus showed, that even the same kind of biomass (corn in this case) causes different results during gasification depending on the exact species and the conditions of growth of the crops [20]. For aqueous feeds like sewage sludge, pyroligneous acid, but also algae gasification in supercritical water seems to be more suitable for gasification as no further water has to be added to the reaction mixture.

### 3.3 Apparatus

For laboratory scale experiments three different kinds of reactors are reported in literature: batch reactor (e.g. quartz capillary tubes [5, 16]), semi-batch reactor (e.g. continuously stirred tank reactor CSTR [19]) and continuous reactor (e.g. plug flow reactor PFR [3, 21]). Most of the materials of construction have an influence on the experimental results. The only reactor material reported in literature which seems to be inert under the reaction conditions of supercritical gasification is quartz. Typical material of construction for reactors dealing with supercritical water are nickel base alloys like Inconel and Hastelloy. The yields of all gases, especially the yield of hydrogen were higher in a reactor made out of Inconel compared to reactions performed in a reactor which was made out of Hastelloy [3].

The pilot plant VERENA of the Karlsruhe Institute of Technology (KIT) allows experiments with a maximum throughput of 100kg/h, at up to 700°C and 35 MPa [22, 23]. Both agricultural wastes (herbage [21]) and industrial wastes (pyroligneous acid [22]) as well as feeds which could be used as feed for animal (corn silage [22]) or as direct fuel (ethanol [22]) have been successfully converted.

### 3.4 Catalysis

Resende et al. studied the effect of metals as catalyst for the gasification of cellulose and lignin in supercritical water [24]. All metals which have been applied (Nickel, Copper, Iron and Ruthenium) showed for cellulose and lignin (Ruthenium was not examined) higher hydrogen yields. Similar results found Chakinala et al. for SCWG of algae with the addition of different metals [16]. All used catalyst (Inconel powder, NiMo, Ni wire, CoMo, Ru/TiO₂, PtPd) increased the gasification efficiency, especially the Ru/TiO₂ catalyst, with which a yield of hydrogen of 100% was reached. DiLeo observed deactivation of the nickel catalyst during experiments with methanol as feed [25].

Catalysts which consisted of different kinds of carbon were described by Xu et al. [26]. They used different carbon sources as coconut shell, charcoal, coal and macadamia shell and feeds like cellulose, glycerol, bagasse liquid extract and sewage sludge. For all feeds and catalysts they found an improvement of the gasification results. After less than 4 hours deactivation of the carbon as catalyst was observed.

Besides the heterogeneous catalysis of metals and carbon described above, alkali are known for their catalytic properties. After addition of KOH or K₂CO₃ a product gas rich in hydrogen and carbon dioxide is obtained, because the water-gas shift reaction is catalysed by potassium [27]. This can be applied to carbohydrates, aromatic compounds, glycine and real biomass. Pyrocatechol, a model substance for lignin, is also almost completely gasified in the presence of KOH [28]. Also Na₂CO₃ is well known for catalytic effects during cellulose gasification, which result in a higher gasification efficiency [29].

### 3.5 Other factors influencing the supercritical gasification of biomass

Besides the parameters already discussed as temperature, reaction time, concentration, heterogeneous and homogeneous catalysis, also the heating rate of the biomass seems to influence the gas yield. Matsumura et al. found a higher gasification efficiency at higher heating rates without changes in the gas composition [30]. Sinag et al. studied the influence on the formation of intermediates and detected a lower influence of catalysts on gas formation at higher heating rates [31].
D’Jesus et al. studied the influence of the particle size of the feed materials to the supercritical water gasification with corn silage [20]. They found a higher hydrogen yield for finer particles and a conversion which increased by 20% due to a decrease in particle size by 50%.

4. Conclusion and prospect
Gasification of biomass in supercritical water is a promising technology for the future [32-35]. The properties of supercritical water allow decomposition of organic matter at high rates. Waste streams of biomass or aqueous biomass like algae can be processed. The product gas consisting mainly of hydrogen, methane and carbon dioxide is generated at high pressure, which allows further utilisation of the product gases without compression.

Evaluation of the process showed a lower environmental impact potential than anaerobic fermentation in case of a combined production of hydrogen and methane [36]. On the other hand the costs of the product gas are still higher than other already available fuel gases [37]. Calzavara et al. pointed out, that the recovery of the process water is an important factor for the efficiency of the process [38]. Gasafi et al. concluded, that sewage sludge may be a potential market for SCWG [39].

The utilisation of solar energy as heat source for supercritical water gasification may be the next step to make this process even more sustainable [40].

References


