

Biomass gasification in supercritical water: Key compounds as a tool to understand the influence of biomass components.

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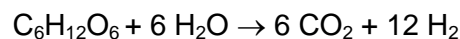
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Introduction

Difficult access to fossil energy sources today has already resulted in increased costs of e.g. petroleum, although petroleum resources have not yet been exhausted. The reason does not only lie in the limited availability of fossil energy sources. But it demonstrates that it is necessary to explore alternative energy sources. One of these energy sources is biomass. The use of biomass as an energy source also is “CO₂-neutral”, as growing plants take up as much CO₂ as is released during use. As both processes, formation and use, take place on the same time scale contrary to fossil fuels, therefore CO₂ emission is not increased by the use of biomass.

In Germany, the potential share of biomass in primary energy supply is estimated to amount to about 5 – 10 %. Present use of biomass, however, mainly focuses on dry wood for energy supply. About 1.6 % of the primary energy consumption is covered by dry wood mainly [Staiß 2002]. In Germany, about 70 – 80 million t of biomass (dry matter,[Leible 2000]) remain unused. This so far unused biomass mainly comprises “wet biomass”, i.e. biomass with a water fraction in excess of 50 %, mostly above 80 %. Often, these wet biomass residues have to be disposed of at considerable costs, as they can no longer be spread on fields due to stricter legal regulations. Apart from cellulose and hemicellulose, this wet biomass does not contain any lignin unlike woody biomasses, but has a much higher salt content. Furthermore, these residues may contain proteins. Consequently, the work described here focused on the influence of proteins and salts on the decomposition of cellulose as a main constituent of the biomass.

The wet biomass may be dried and combusted or gasified by a “dry process”. However, drying is associated with considerable costs at such a high water content. Biomass may also be converted into methane by fermentation. This, however, requires a certain nutrient composition and the absence of poisons. Moreover, the conversion remains incomplete. The work described here was aimed at generating hydrogen from wet residual biomass using the water contained as a reaction medium and reaction partner (see below). Hydrogen is considered a potential “secondary fuel of the future” and may be used in e.g. fuel cells for electricity generation or for syntheses of e.g. synthetic fuels. The water contained in the biomass acts as both reaction medium and reaction partner during gasification in supercritical water. Under the reaction conditions, the biomass reacts with water, thus forming hydrogen and carbon dioxide. About half of the hydrogen formed originates from the water. The – stoichiometrically possible - maximum hydrogen yield from biomass may be formulated as follows when using glucose as a model substance for the biomass:



Mostly, the hydrogen yield is smaller, as varying amounts of methane are formed depending on the reaction conditions and the initial substance used.

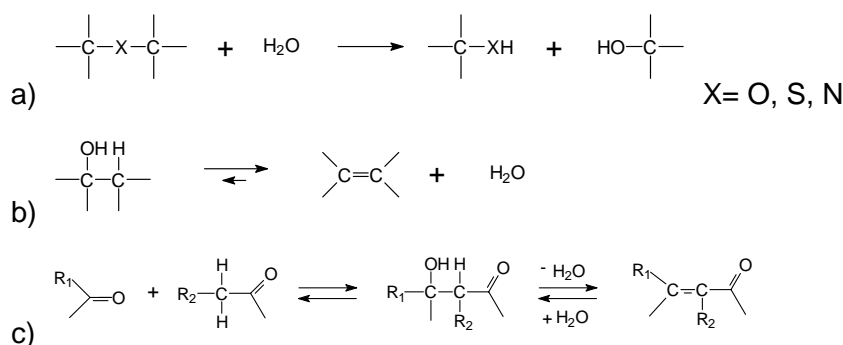


Fig. 1: Reactions of biomass, biomass model compounds and their consecutive products accelerated in near-critical water: Hydrolyses (a), water elimination (b), aldol cleavages, and aldol condensations (c).

The properties of near-critical and supercritical water differ from those of water under normal conditions. In addition, they vary strongly as a function of temperature and density. At increased temperatures and below the critical point, for instance, the ion product of water is higher by about four orders of magnitude than under normal conditions. As a consequence, reactions that normally require the addition of either acids or bases now reach high reaction rates even without the above additions. As far as the conversion of biomass is concerned, this means that e. g. hydrolyses, water cleavages, aldol cleavages, and aldol condensations (see Fig. 1) take place very rapidly in this range and lead to a large number of products. Above the critical point, the relative static dielectric constant decreases very strongly. Here, water possesses the properties of a non-polar solvent. For this reason, gases and most organic substances are dissolved excellently in supercritical water, while salts are less soluble. These special properties result in a number of advantages of gasification in supercritical water as compared to “dry gasification processes”:

1. Less tar and coke are formed. As the biomass is decomposed very rapidly by hydrolysis and the cleavage products of the biomass are dissolved in the supercritical water, less polymerisation reactions take place than in the solid-gas systems obtained from dry processes. In the latter case, the local concentration of polymerisable substances on/in the solid is very high. Accordingly, they may polymerise very rapidly.
2. At very small CO contents (typically < 1 vol.% of the product gas), a high H₂ yield can be reached. This is a result of the reaction of the biomass with water at a high water excess (see above).
3. H₂ may be obtained under pressure. It is not necessary to compress H₂ e.g. for transportation.
4. CO₂, the second main product apart from H₂, can be separated easily, as the solubility of CO₂ in water under pressure and at room temperature is much better than the solubility of H₂.
5. The high space-time yield results from the use of a high-pressure process with an accordingly increased density and from the high reactivity of the biomass under these conditions.
6. No drying of the “wet biomass” is necessary.
7. Inorganic constituents are not volatile, but remain in the aqueous solution. This prevents corrosion effects along the gas path, which were found to be very problematic when using dry processes with salt-rich biomass [Chen 2004, Blander 1999].

To produce a maximum amount of hydrogen from wet biomass of varying compositions, it is required to know and understand the major chemical processes. It is important how these

processes are influenced by constituents or additions and how e.g. selectivity for hydrogen production may be increased.

As biomass is a complex mixture of variable composition, it is very difficult to identify individual reaction paths. For this reason, experiments were carried out with model substances like glucose [Sinag 2003, Sinag 2004a, Sinag 2004b], glycerol [Bühler 2002] or pyrocatechol [Kruse 2000] first. Key substances, usually typical intermediate products, were allocated to each reaction path identified as “indicators” (Fig. 2; [Kruse 2003a, Kruse 1999, Sinag 2003, Sinag 2004a, Sinag 2004b]). With the help of these key substances, these reaction paths were identified again in the conversion of biomass. Variations of the concentrations of key substances indicate a changed selectivity of the respective reaction path, e.g. due to salts.

Individual reaction paths and their key substances as well as the influence of salts on these reaction paths shall be discussed below. After that, the influence of proteins contained in the biomass as well as of heating shall be illustrated. The results will give rise to approaches to optimising the reactor concept.

Experimental Set-up

The experiments were carried out using three different reactors: An tumbling batch reactor (1 l inner volume, up to 500°C, 50 MPa; [Sinag 2004a]), a spiral tubular reactor (6 m long, about 20 ml inner volume, up to 600°C, 30 MPa; [Sinag 2003]), and a continuous stirred tank reactor (CSTR about 190 ml inner volume, up to 600°C, 100 MPa; [Sinag 2004b]). These three reactors correspond to the three classical types of reactors used in reaction technology and do not only differ by the reaction times reached, but also by the back-mixing and heating rates.

Results and Discussion

The first reaction step (see Fig. 2) is the hydrolysis of cellulose, the main constituent of biomass, to sugar units. This reaction step is very fast [Sasaki 1998, Sasaki 2004]. From sugars, e.g. glucose or fructose, furfurals may be formed by multiple water cleavage [Antal, Jr. 1990, Srokol 2004]. The key substances for this reaction path are 5-hydroxymethylfurfural (HMF), methylfurfural (MF), and furfural (FU). Their concentrations are particularly high in the subcritical range and in the presence of acids (see e. g. [Kruse 2003a]). But also at higher temperatures and short residence times, these substances can be detected. It is demonstrated by experiments using glucose in the tubular reactor at 400 °C (Fig. 3, [Sinag 2003]) that the addition of KHCO_3 leads to a significant reduction of the furfural concentration measured. If possible, furfural formation should be reduced, as furfurals polymerise easily and the thus formed solids react further very slowly only. The reduced coke formation that is also observed (only in the batch-type reactor, see below and [Sinag 2004a]) in the presence of alkali salts may possibly be attributed to a reduced formation of furfurals and other polymerisable, unsaturated compounds. Both sugars and furfurals may form smaller molecules, above all short-chained aldehydes and acids that are partly unsaturated (Fig. 2). These reaction steps may be an aldol cleavage of the sugars [Kabyemela 1999, Kabyemela 1997, Srokol 2004] or an acid cleavage of furfurals [Luijckx 1994]. The key substances for these reaction paths are e.g. formic acid, acetic acid, and laevulinic acid as well as formaldehyde and acetaldehyde. From these low-molecular intermediate products, gases and molecules of higher molar mass may form. The experimental finding of phenol formation having a reaction order close to 2 among others allows the assumption to be made that the phenols detected are at least partly formed from smaller fragments by a ring closure reaction [Kruse 2003b]. According to studies performed in a batch-type reactor with glucose at 500°C [Sinag 2004a], the addition of alkali salts causes the phenol concentration to be increased slightly (Fig. 4).

The addition of alkali salts strongly affects the gas composition, as was demonstrated by the use of various model substances (Fig. 5 and Fig. 6). By the addition of alkali salts, the CO yield was reduced drastically, while the yields of CO_2 and H_2 increased accordingly. This

certainly is a result of the catalysis of the water-gas shift reaction by alkali salts [Elliot D.C. 1983].

Water-gas shift reaction: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$

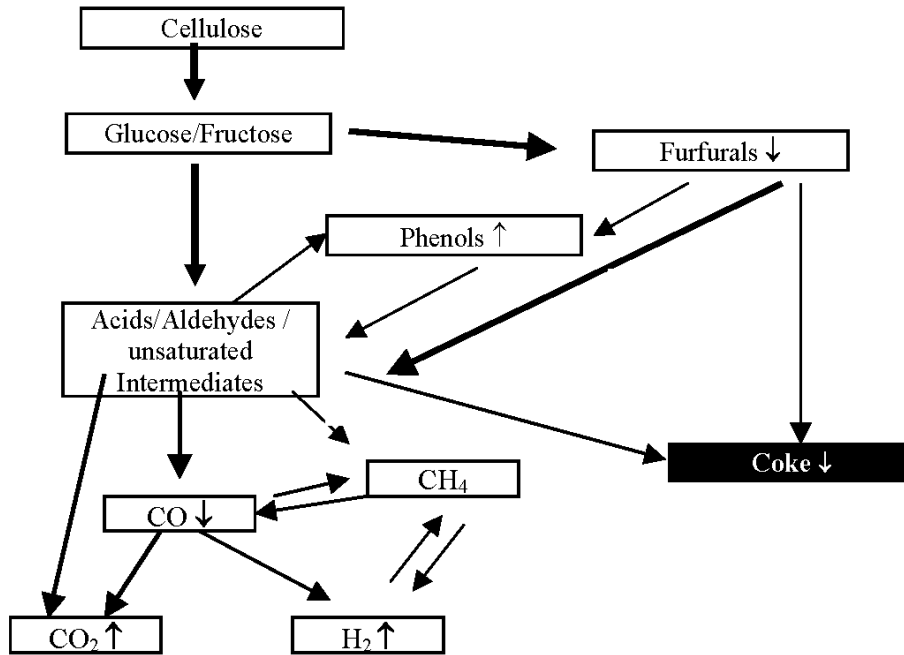


Fig. 2: Simplified reaction mechanism starting from cellulose. The short arrows near the key substances indicate the changes due to the addition of potassium salts.

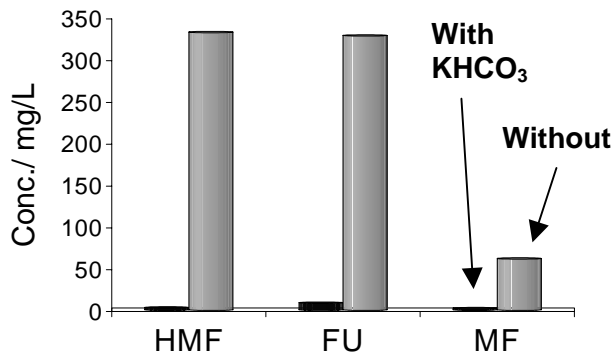


Fig. 3: Concentration of 5-hydroxymethylfurfural (HMF), methylfurfural (MF), and furfural (FU) after reaction of glucose with and without KHCO_3 (tubular reactor; 400 °C, 25 MPa, 16 s, 1,5 % (g/g) Glucose, 0,2 % (g/g) KHCO_3 ; [Sinag 2003])

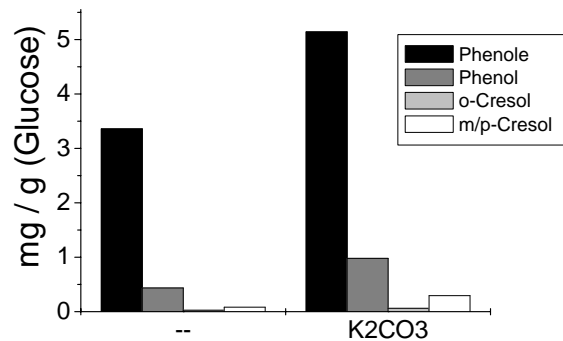


Fig. 4: Concentration of all phenols (phenols index), and selected single phenols after reaction of glucose with and without K_2CO_3 (batch reactor heated up to 500 °C (32 MPa) with 1 K/min, 7,5 % (g/g) Glucose [Sinag 2004a])

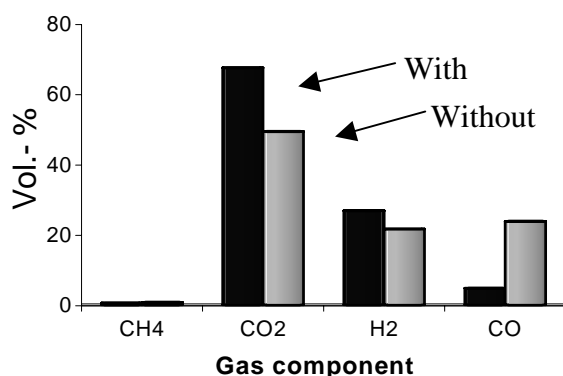


Fig. 5: Composition of the gas phase after reaction of glucose with and without KHCO₃ (tubular reactor; 400 °C, 25 MPa, 16 s, 1,5% (g/g) Glucose, 0,2 % (g/g) KHCO₃; [Sinag 2003]),

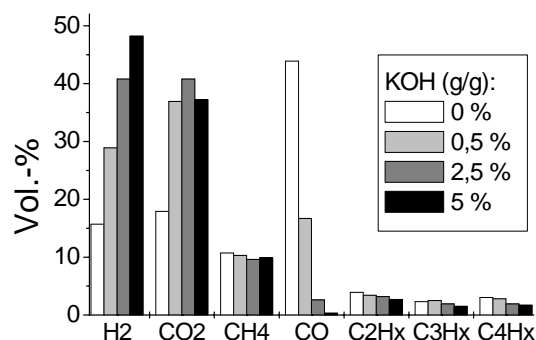


Fig. 6: Composition of the gas phase after reaction of pyrocatechol with various amount of KOH (batch reactor heated up to 500°C (25 MPa), 5 % (g/g) pyrocatechol; [Kruse 2000])

It is obvious from the results presented that various reaction steps of biomass decomposition are influenced by potassium salts. The reasons are not yet understood. There is experimental evidence, however, that these effects are closely linked with the catalysis of the water-gas shift reaction by alkali salts [Kruse 2005]. Apparently, not only the gas composition, but other reaction paths also may be affected by the occurrence of reactive intermediate stages of the water-gas shift reaction or by hydrogen in statu nascendi as “active hydrogen”. In the experiments with glucose and other model substances for biomass, the potassium salts were added, because “wet biomass” as the initial product desired for gasification possesses a fairly high salt content and no information was available on how these salts act on biomass decomposition. The question now arising is whether the salts in real biomass actually have an effect similar to that of KHCO₃ or K₂CO₃ and whether the cellulose of the biomass shows a behaviour similar to that of glucose under the experimental conditions. This question may be settled by comparative experiments with biomass only.

Experiments with real biomass are difficult to perform. A reproducible composition and good mixing must be ensured. To ensure pump ability in spite of the relatively small pipe cross sections of the laboratory facilities, the fibrous biomass must be ground finely. For the work presented here, a pap made of carrots and potatoes was used (from the Hipp company). This vegetable biomass (phytomass) does not contain any lignin and its composition corresponds to the formula of CH_{1,87}O_{0,98}N_{0,02}S_{0,001}. This biomass has a dry matter content of 10.8% and a potassium content of 1241 mg/kg.

The differing concentrations of the key substances reflect varying selectivities of the reaction paths. Figure 7 shows the concentrations of HMF, total phenol, phenol, formic acid, and acetic acid of phytomass, glucose, and glucose/K₂CO₃ following reactions under the same experimental conditions. As already mentioned, the addition of alkali salts reduces furfural concentration. Similar to glucose/K₂CO₃, the phytomass possesses very small furfural concentrations. The total phenol concentration of the phytomass is somewhat higher than after the conversion of glucose, but not as high as for the glucose/K₂CO₃ system. From this, it may be concluded that the behaviour of alkali salts in the biomass is similar to that of added potassium salt and that glucose/K₂CO₃ is a good model system for salt-rich biomass. Differences of these two educts in terms of the formic acid concentration should be neglected, as liquid chromatography of formic acid is very matrix-sensitive due to its instability and the strongly varying stabilities of various formates. As the biomass also contains other salts in addition to alkali salts, various formic acid concentrations may result even without modifications of the chemical gasification process.

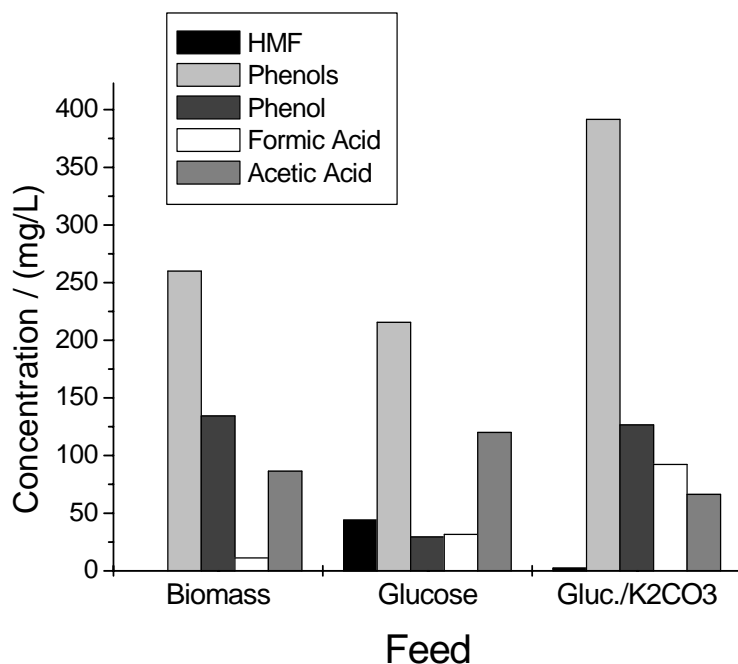


Fig. 7: “Fingerprints” of various initial substances: Concentrations of selected key substances following the conversion of phytomass, glucose, and glucose/K₂CO₃ (batch-type reactor, heating to 500°C, and 1 h reaction at 500°C, 5% dry matter content, if applicable, 0.5 % (g/g) K₂CO₃).

In spite of all differences, it is surprising why the “fingerprints” of the different model substances are so similar. The phytomass is a solid and in both other cases, solutions are fed into the reactor. In addition, the composition of the biomass is completely different. It mainly consists of cellulose, and not of glucose. Apart from alkali salts, also other salts exist, but not in the form of carbonates. The similarity of the chemical processes in spite of the varying compositions demonstrates that the first step of biomass decomposition, namely, the hydrolysis of the cellulose, must be a very fast reaction. Consequently, cellulose exhibits a behaviour that is very similar to that of the model substance glucose. This very rapid decomposition of polymer biomass structures is the major difference from “dry biomass gasification processes”.

Many residual biomasses that may be applied as initial substances for gasification in supercritical water contain proteins. To study the influence of proteins, a new model biomass was selected. It contains chicken and rice (pap by the Hipp company), i.e. also animal constituents (zoomass). It also does not contain any lignin, but the contents of nitrogen and sulphur are much higher than those of the phytomass. The chemical composition corresponds to the formula of CH_{2.06}O_{0.52}N_{0.12}S_{0.01}. The zoomass has a dry matter content of 17.7% and a potassium content of 1634 mg/kg. Comparative studies revealed clear differences from other model systems.

When comparing the gas yields of conversions under analogue reaction conditions in the continuous stirring vessel (Fig. 8), it is found that those of glucose/K₂CO₃ and phytomass are very similar. The gas yield of the zoomass is much smaller. After a reaction time of 5 minutes, however, the gas composition of the product gas is about identical in all three cases. The CO content is ≤ 0.3 vol. %, the CH₄ content is 14-15 vol. % and the H₂ content is 40-47 vol. %; the rest is CO₂. The negative effect of the proteins contained may be compensated by the addition of K₂CO₃, as is obvious from Fig. 9. Here, the product gas also contains more hydrogen after the addition of K₂CO₃.

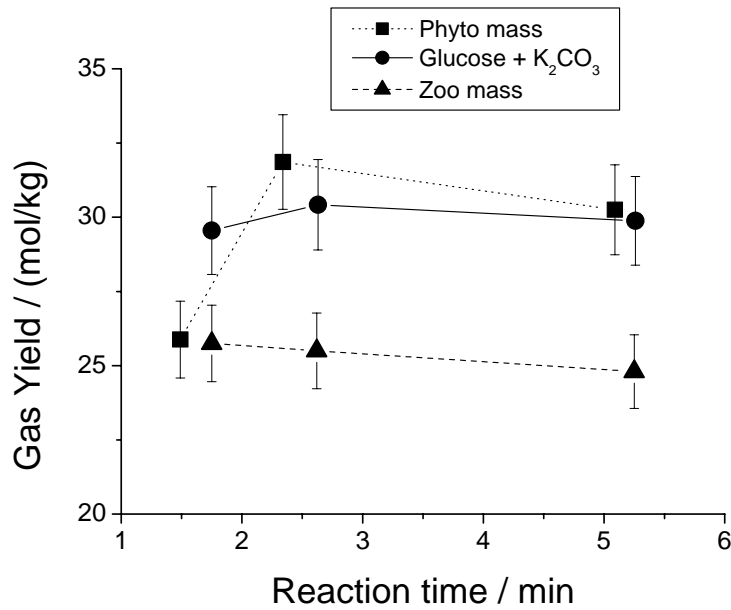


Fig. 8: Gas yields as a function of the residence time after the conversion of phytomass, glucose with K₂CO₃ (0.5 % (g/g)), and zoomass (CSTR, 5% dry matter content, 500°C, 30 MPa).

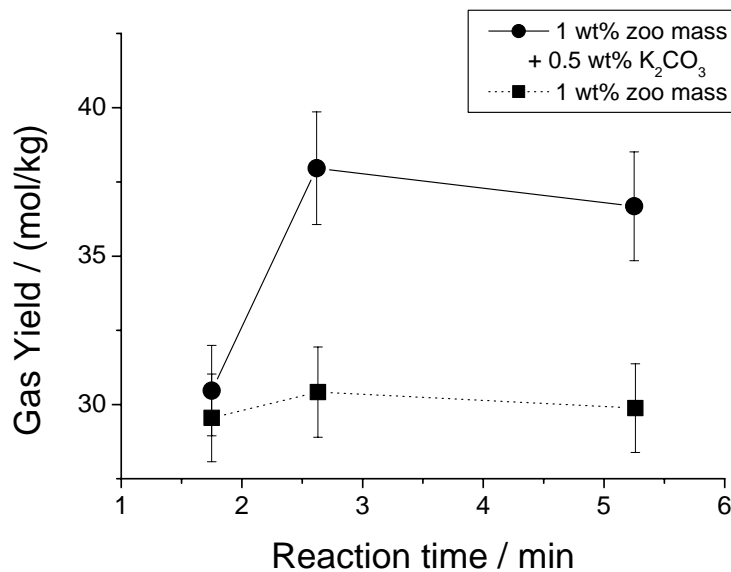


Fig. 9: Gas yields as a function of the residence time after the conversion of zoo-mass and zoomass with K₂CO₃ (0.5 % (g/g)) (CSTR, 1% dry matter content, 500°C, 30 MPa).

Interesting findings were also obtained from the comparison of the results achieved with various reactors. For instance, very small amounts of coke were found for each gasification experiment in the batch-type reactor. In the continuous stirring vessel, coke was never found, irrespective of the initial product used. In the tubular reactor, experiments were carried out with model substances only and no coke formation was observed. As the biomass or model substance are heated relatively rapidly in the tubular reactor and in particular in the

continuous stirring vessel – here, heating takes place nearly promptly by the mixing of the cold educt with the hot reactor contents – and heating in the batch-type reactor is relatively slow (1 or 3 K/min), it may be assumed that the heating rate is of decisive importance to coke formation. A possible explanation is that at lower temperatures and sufficiently high residence times, many compounds with double bonds are formed under subcritical conditions. These also include e. g. furfurals and others that polymerise with increasing temperature and starting radical formation. This effect could be enhanced by a phase separation in the subcritical range, as it was predicted for these conditions [Feng 2004]. In this case, the polymerisation rate in the organics-rich phase would be much faster than in a homogeneous mixture due to the concentration effect. Most probably, the relatively good gasification results obtained in a continuous stirring vessel with respect to residual carbon and gas yield may not only be attributed to rapid heating. Due to back-mixing, for instance, the “active hydrogen” formed by the water-gas shift reaction could be effective in each reaction step and not only at the end of the reaction chain as it is the case in reactions without back-mixing. Hydrogen is a late consecutive product of biomass gasification (see Fig. 2)! This assumption is supported by the fact that gasification only is enhanced in batch-type experiments when CO is compressed at the beginning of the reaction for the water-gas shift reaction to take place [Kruse 2005]. Obviously, this results in an inhibition of polymerisation and a promotion of cleavage, as it is known from liquefaction processes with “active hydrogen”. This can be used to optimise the gasification result.

In addition to the laboratory facilities, a pilot plant was built at the Institute for Technical Chemistry of Forschungszentrum Karlsruhe (design data: Up to 700°C, 35 MPa, 100 kg/h at up to 20% dry matter content) [Boukris 2004]. It is the only plant of its type, and first results are very promising. Major components, such as the heat exchanger, the pumps, and the hydrogen separation system, have already demonstrated their functionality and high efficiency.

Conclusions

It is demonstrated by the studies performed that the salts contained in wet biomass have a major influence on the chemical processes. This influence is mainly positive. Alkali salts increase the hydrogen yield and reduce coke formation. A drawback is the increase in the phenol formation that, however, is not very pronounced. The same effect may be reached by the addition of alkali salts, e.g. K_2CO_3 and $KHCO_3$. When using biomass with a low salt content and protein-containing biomass, such alkali salts should be added to increase the hydrogen yield. It would also be advantageous to heat the biomass as rapidly as possible. Heating, however, is subject to technical limits. It is recommended to integrate a heat exchanger for an efficient use of the heat. The fresh biomass then is heated in a counterflow heat exchanger by the effluent leaving the reactor [Boukris 2004]. In this case, the heating rate is defined by the heat exchanger and not very high. Back-mixing also is favourable to make use of the effect of the “active hydrogen”. The good results obtained with the pilot plant show that the process can also be implemented on a large technical scale.

Outlook

To study the effects of the optimisation approaches mentioned above, a stirring vessel was coupled with a tubular reactor. In the stirring vessel, the cold biomass is heated up abruptly by mixing with the hot reactor contents. Moreover, back-mixing allows for a good distribution of the “active hydrogen”. The dilution effect of back-mixing additionally prevents phenol formation, the reaction order of which is relatively high. A tubular reactor is installed downstream of the stirring vessel. Here, the remaining intermediate products are converted into gases.

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