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Energy Recovery from Wet Biomass Feedstock in Supercritical Water

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Summary

Results of hydrothermal and oxidative experiments with glucose as a model substance for cellulosic biomass in sub- and supercritical water at 24 - 34 MPa, 250 - 480 °C and 2 - 35 s are presented. In presence of stoichiometric oxygen concentration (for total oxidation to CO_2 and H_2O) Glucose decomposes already at subcritical temperatures readily to CO and low molecular liquid substances, chiefly organic acids. In turn these are in general more stable and react only slowly with oxygen. Glucose decomposition followed with and without oxygen a simple first order rate law. Different technical process designs of a SCWO (supercritical water oxidation) plant for energy recovery from wet biomass are discussed.

Introduction

Energy recovery from biomass spares fossil fuels and, since it represents a CO_2-neutral energy feedstock, it can make an import contribution to climate protection. Large, till now on technical scale virtually unused resources are wet waste biomass with > 50 % (g g^{-1}) moisture, originating from the agricultural, the municipal and the industrial sector (FZK 1997). Total oxidation of wet biomass in supercritical water seems to be a promising alternative to the conventional combustion with preceding drying of the biomass. Above its critical conditions (i.e. 22.1 MPa and 374 °C) water exists only as a fluid, the distinction between vapour and liquid vanishes and therefore the energy of vaporisation has not to be provided. To be more precise, starting from water under ambient conditions in total a comparable amount of energy has to be provided to attain the supercritical state of water by increasing pressure and temperature. However, this energy can be recovered by a heat exchanger after the reactor and be utilised to heat up the feed stream. Thereby the net amount of energy is much lower than the energy of vaporisation.

In conventional combustion technology a complete heat recovery cannot be employed for economic reasons and fuel moisture leads to energy loss by vapour leaving in flue gases. Solid fuel combustion operates at ambient pressure and so volumetric flows are high, leading to large dimensions of combustion chamber and flue gas funnel. Therefore a heat exchanger for water condensation and recovery of the energy of vaporisation would be of large size as well and is uneconomical, since it must be build of expensive corrosive resistant steel and energy is recovered at an unattractively low temperature-level of 100 °C.

An oxidation in supercritical water shows further advantages as extremely low levels of noxious emissions like NO_x and SO_2 (Schmieder and Abeln 1999). In order to optimise process parameters, e. g. temperature, pressure and oxygen concentration, and to clarify the feasibility of such a SCWO process, knowledge of the kinetics and mechanism of biomass oxidation in sub- and supercritical water is needed. As a model substance for cellulosic materials glucose was investigated, since under sub- and supercritical conditions the glycosidic link breaks easily (Sasaki *et al.* 1998).

Experimental

Measurements are carried out in a **continuous high pressure plant** (see Figure 1) with a gradient free jet loop reactor (*V* = 16 mL) made of Inconel 625. Passing through a nozzle in the top of the reactor, the entering feed streams downwards in the interior of an insertion tube, then turns round at the bottom and passes upwards through the annular gap. Under-pressure arising at the jet entrance forces the reaction mixture downwards again and generates thorough mixing by a circulating flow. The oxygen source is an aqueous solution of hydrogen peroxide, which decomposes completely in a tubular heater at 250 °C into oxygen and water. High pressure diaphragm pumps are used for the transport of the hydrogen peroxide solution (for hydrothermal experiments: only deionised water) and the aqueous glucose solution. The oxygen enriched water stream passes in coiled tubes a pre-heater, consisting of a molten salt bath (potassium nitrate / sodium nitrite at 1 / 1 ($g\ g^{-1}$)), and is mixed with the cold glucose solution stream directly before reaching the jet loop reactor. Thereby a fast heating of glucose and a defined reaction starting point is ensured.

After leaving the reactor the reaction mixture is immediately cooled and then decompressed to ambient pressure by a relief valve (Swagelok, SS-4R3A5-R). The gaseous and liquid phases are cooled down to 10 - 15 °C and separated from each other for analysis. Residence time behaviour experiments by Bröll (2001) showed that the jet loop reactor can be assumed to be a continuously stirred tank reactor (CSTR).

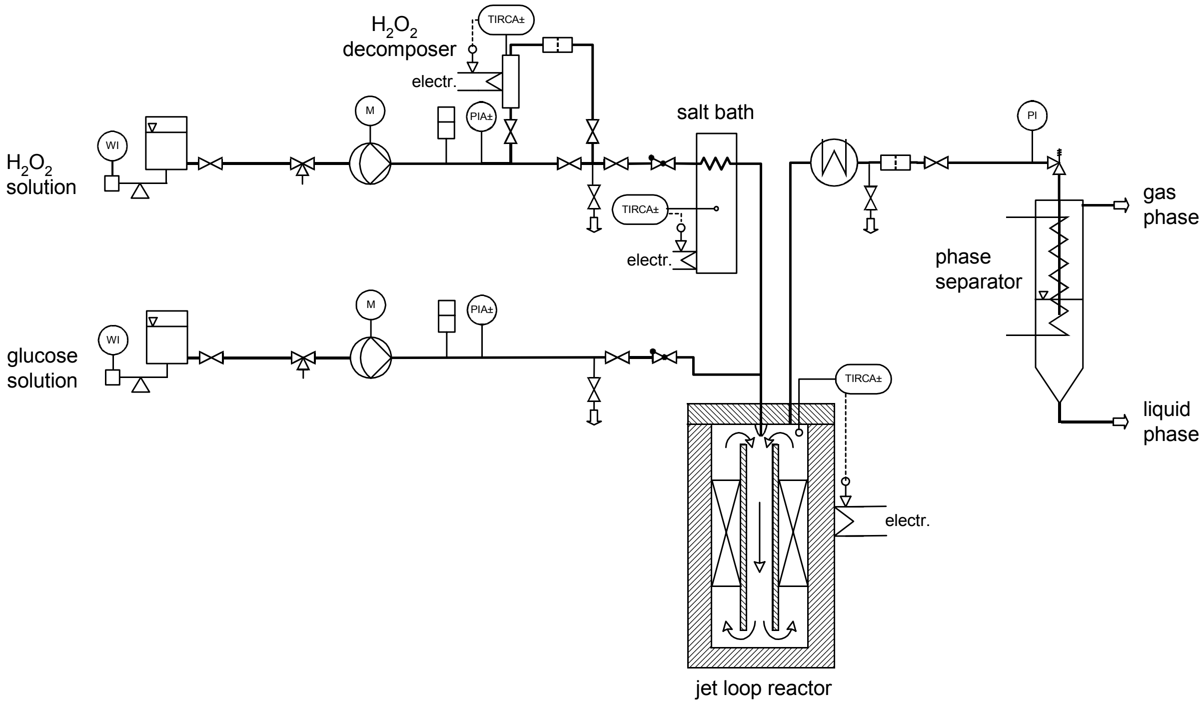

Figure 1: Continuous high pressure plant. In hydrothermal experiments the H_2O_2 solution is replaced by deionised water.

The **gaseous reaction products** carbon monoxide, carbon dioxide, and oxygen are analysed directly after separation from the liquid phase. The volume fraction of carbon monoxide and carbon dioxide is detected with an infrared absorptiometer (Hartmann & Braun, Uras 14), the volume fraction of oxygen with a magneto-mechanic oxygen analyser (Hartmann & Braun, Magnos 16). Gas flow is measured by a bubble flow-meter.

A quantitative analysis of the **liquid reactor discharge** was done by HPLC (Model ProStar 210, Varian). A cation exchanger column (ION-300H, Interaction Chromatography, Inc.) was operated at 25 °C for the hydrolysis products and 58 °C for the oxidation products, the RI-Detector's temperature was set at 40 °C. The eluent was 2 mM sulphuric acid. Quantified hydrothermal degradation products were: fructose, mannose, 1,6-anhydroglucose, furfural, 5-hydroxymethylfurfural (5-HMF), succinic acid, glyceraldehyde, pyruvaldehyde, lactic acid, hydroxyacetone, glycolaldehyde, glycolic acid, acetic acid, formaldehyde and formic acid. Levulinic acid, xylose and erythrose were only found in small amounts or even traces and not quantified.

Product identification was performed mostly by ^{1}H-NMR (500 MHz, water suppression, lock substance d_6-Acetone). Chemical shift and fine-structure of proton signals gave structural information about the reaction products. Suspected substances were then added in small amounts to reactor effluents and comparison of spectra recorded before and after addition allowed to identify products. Some products showed only ^{1}H-Signals of low intensity or no signal at all, due to low product concentrations (e. g. erythrose) or attenuation by water suppression in case of a chemical shift close to the one of water (e. g. formaldehyde). These were identified via HPLC by varying the column temperature (three different temperatures, e. g. 30, 50 and 58 °C) and injecting a reactor effluent sample and a dilute reference of the suspected substance. A positive identification of a product peak showed for both, sample and reference, good agreement of retention times at all three temperatures. This procedure had to be employed since typical HPLC product chromatograms were quite complex and simple observation of peak signal growth with substance addition (substance spike method) at only one column temperature proved unreliable.

Results

First the **hydrothermal decomposition** of a 0.3 % (g g^{-1}) glucose feed (after mixing) in sub- and supercritical water was investigated at 24 - 34 MPa, 250 - 420 °C and 2 - 35 s. Figures 2 - 5 display conversion X and product yields $Y_{\mathrm{C,i}}$ (carbon basis) with residence time and temperature. These were calculated as follows:

$$X\ /\ \%\ (\mathrm{mol\ mol^{-1}}) = \frac{c_{0,\mathrm{Gluc}} - c_{\mathrm{Gluc}}}{c_{0,\mathrm{Gluc}}} \cdot 100 \tag{1}$$

$$Y_{\mathrm{C,i}}\ /\ \%\ (\mathrm{mol\ mol^{-1}}) = \frac{N_{\mathrm{C,i}}\, c_{\mathrm{i}}}{N_{\mathrm{C,Gluc}}\, c_{0,\mathrm{Gluc}}} \cdot 100 \tag{2}$$

with c_{i} = concentration of compound i and $N_{\mathrm{C,i}}$ = number of carbon atoms per molecule i.

Experiments at supercritical temperatures showed an instable operational behaviour of the plant, which improved with rising pressure. Therefore supercritical experiments were performed at 34 MPa. Since a pressure variation to 34 MPa at subcritical conditions showed no influence on conversions and yields, sub- and supercritical results remain comparable, despite of the different operating pressures. Hydrothermal decomposition proceeds quite fast and at supercritical temperature glucose conversion is virtually complete even at the shortest residence time.

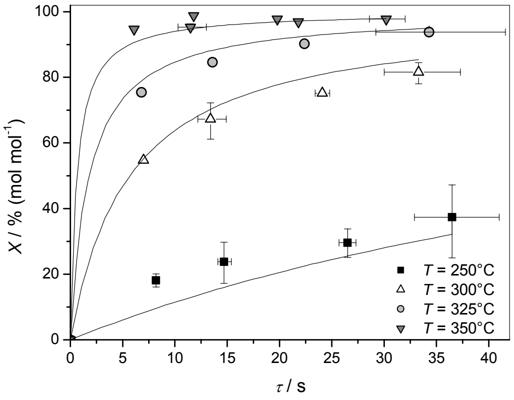

Figure 2: Conversion of glucose at 24 MPa with residence time and temperature. Lines show conversions calculated by a first order reaction model.

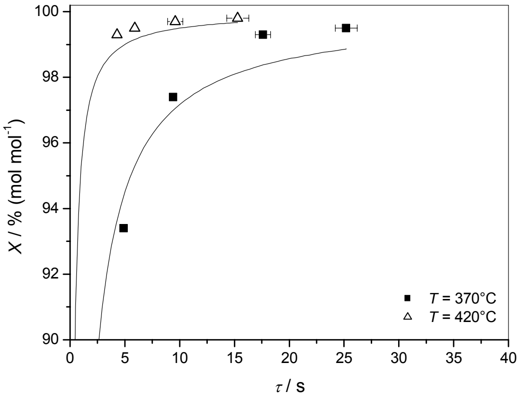

Figure 3: Conversion of glucose at 370 °C, 24 MPa and 420 °C, 34 MPa with residence time. Note the enlarged scale of the conversion axis.

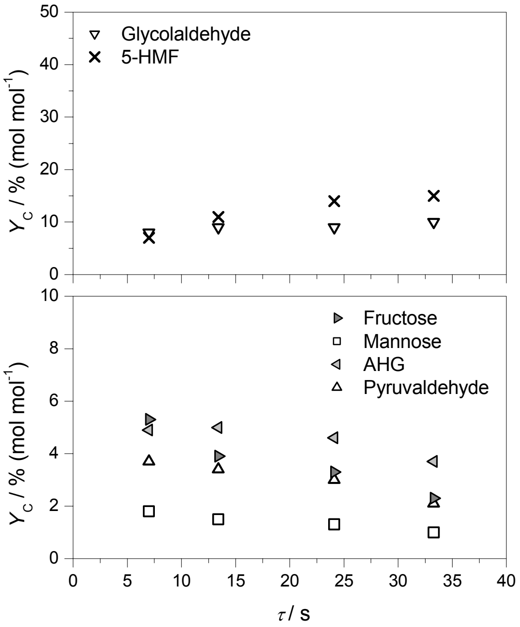

Figure 4: Product yields at 300 °C and 24 MPa with residence time. AHG = 1,6-anhydroglucose. Upper diagram: main products, lower diagram: low-yield products. Note the enlarged scale of the lower yield axis.

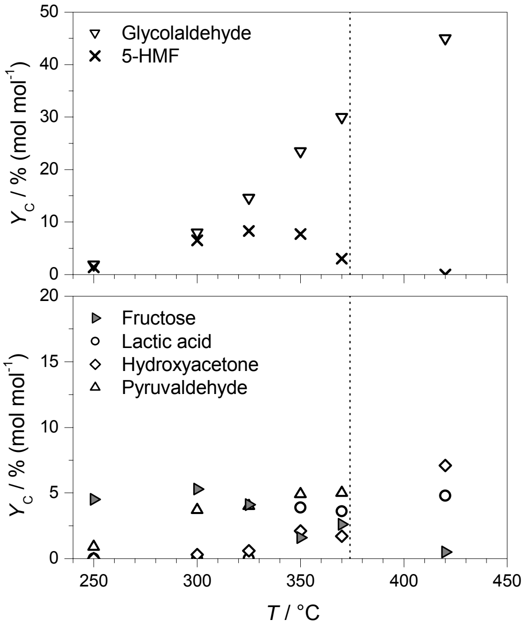

Figure 5: Product yields at 5 - 8 s and 24 MPa (T < 374 °C) / 34 MPa (T > 374 °C) with temperature. Dotted line: critical temperature 374 °C. Not displayed: formic acid and formaldehyde occur in low concentrations, glycolic acid is found above 350 °C.

Based on literature (Antal and Mok 1990, Kabyemela *et al.* 1999, Kirk and Othmer 1965, Modell 1985, Ponder and Richards 1993, Bonn and Bobleter 1983) and own experimental results a reaction network is postulated in Figure 6. At temperatures as low as 200 °C and short residence times glucose isomerizes to fructose and mannose. At slightly higher temperature of 250 °C in addition dehydration to 1,6-anhydroglucose and 5-HMF takes place. 1,6-anhydroglucose is only formed by glucose, 5-HMF by any of the three hexoses (Kabyemela *et al.* 1999). Erythrose and glycolaldehyde as well as glyceraldehyde are formed via retro-adol reactions, respectively. Erythrose and glyceraldehyde themselves are found only in low concentrations and act as intermediates. Erythrose undergoes further fragmentation, probably to glycolaldehyde via retro-aldol reaction, and glyceraldehyde dehydrates via pyruvaldehyde to lactic acid and hydroxyacetone. Glyceraldehyde also equilibrates with its isomer dihydroxyacetone, which is only found in quite small amounts and therefore is omitted in Figure 6.

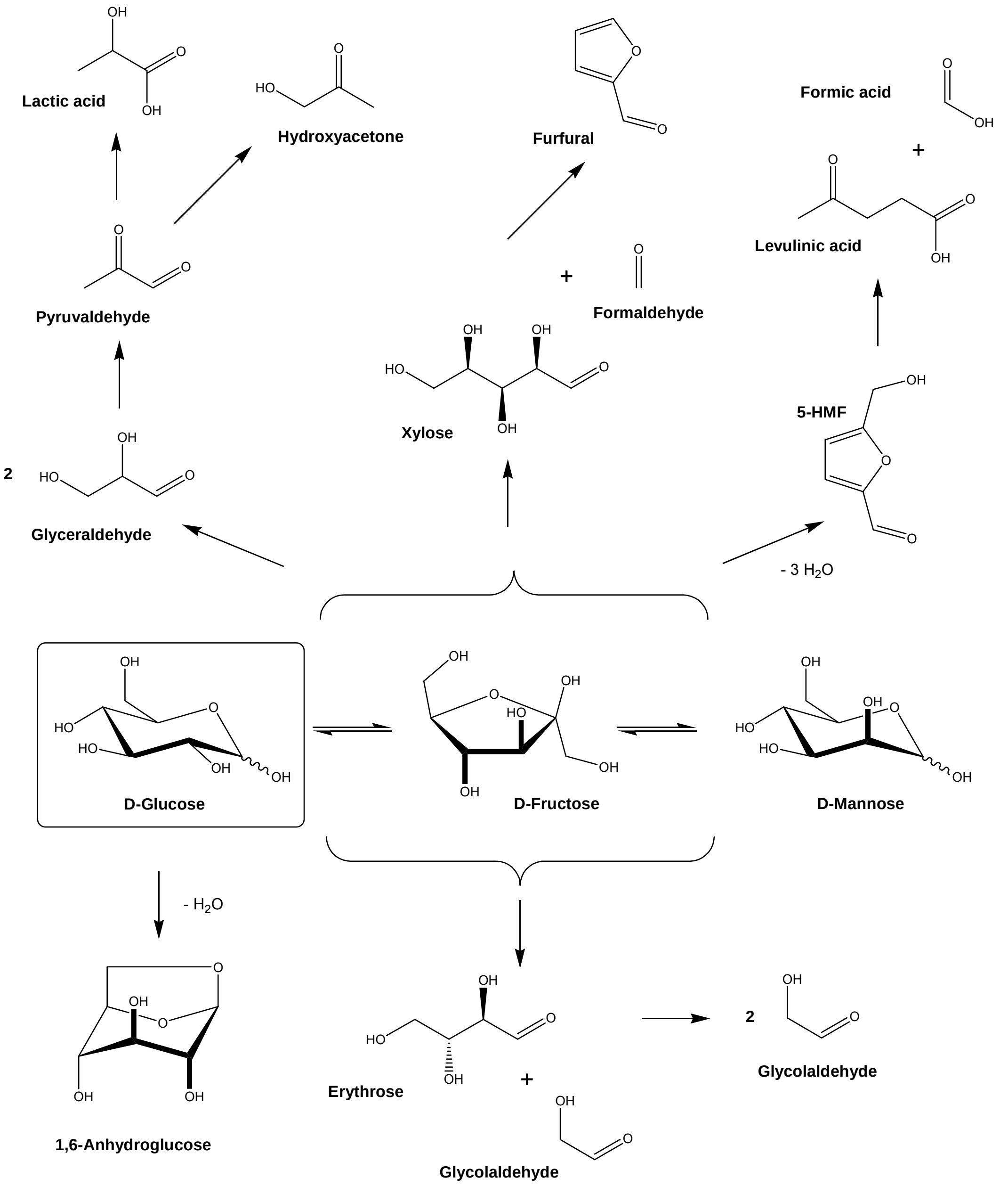

Figure 6: Postulated reaction network for hydrothermal decomposition of glucose. Aldehydes occur in solution actually in hydrate form. Levulinic acid has only been found in traces and seems to be an instable intermediate. This has been observed by Bonn and Bobleter (1983) as well. For reason of clarity not displayed: formed products of the network react further to low molecular weight species as glycolic acid, formic acid, formaldehyde, CO, CO_2 and H_2.

Further increase in temperature promotes the decomposition of the hexoses and their dehydration products 1,6-anhydroglucose and 5-HMF to a multitude of smaller molecules: glycolaldehyde, pyruvaldehyde, hydroxyacetone, glycolic acid, formic acid, formaldehyde, CO, CO_2 and H_2. Moreover at intermediate temperatures of 300 - 370 °C, decomposition of hexoses to xylose occurs, which in turn dehydrates to furfural. As a parasitic side reaction at all temperatures brown humin polymers are formed. Since these are not analysed, carbon balance closure is in general with 58 - 83 % (except at 250 °C: 87 - 94 % due to low glucose conversion) quite poor. Some smaller peaks in HPLC chromatograms could not be identified and contribute to carbon loss as well.

Then **oxidation experiments** with the same 0.3 % (g g^{-1}) glucose feed and stoichiometric amounts of molecular oxygen, according to eq. (3), were performed at similar reaction conditions. As a surprising result, the presence of oxygen had no influence on the decomposition rate of glucose. The conversion (Figure 7) is the same as in the hydrothermal experiments.

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O \qquad (3)$$

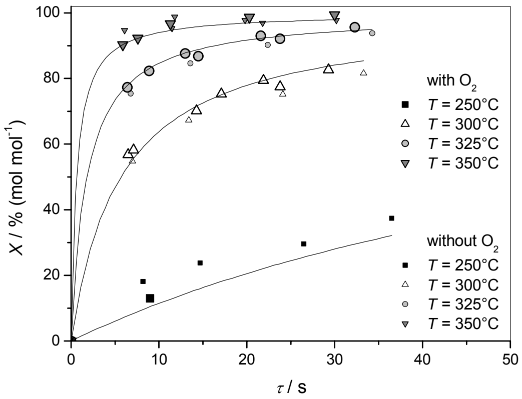

Figure 7: Effect of Oxygen on conversion of glucose at 24 MPa with residence time and temperature. Lines show conversions calculated by a first order reaction model. Large symbols: experiments with stoichiometric oxygen supply, small symbols: hydrothermal experiments.

In contrary product yields changed substantially with stoichiometric oxygen concentration. Main products were oxigenates as formic acid, CO and CO_2. Figures 8 and 9 give an impression of the products obtained at different residence times and temperatures. Therefore the decomposition of glucose in presence of oxygen proceeds first via steps of hydrothermal decomposition. Not glucose but intermediate hydrothermal products react with oxygen to form chiefly CO_2, CO and formic acid. The obtained experimental results are illustrated as a reaction scheme in Figure 10. Formic acid is unstable at temperatures above 400 °C (Krammer 1998). Nevertheless at supercritical temperatures it is present in relative high concentrations in reactor effluents, indicating its importance as an intermediate of oxidative decomposition. Under experimental conditions formed CO reacts only slowly to CO_2, above all via direct oxidation (Holgate *et al.* 1992, Sato *et al.* 2004). The water gas shift reaction of CO and water to CO_2 and H_2 occurs only to negligible extend.

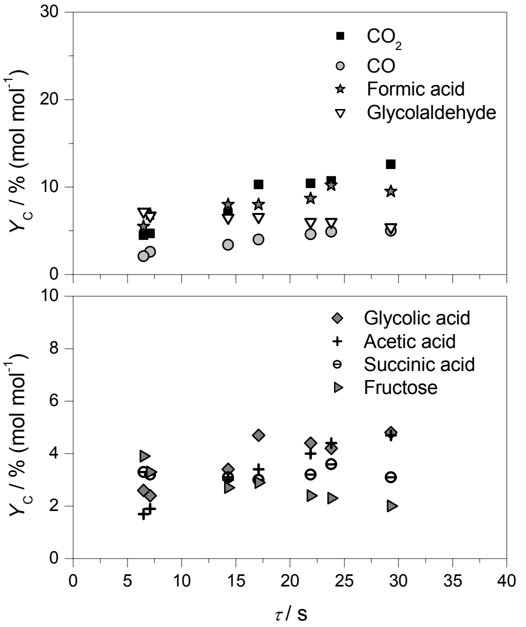

Figure 8: Product yields at 300 °C, 24 MPa and stoichiometric oxygen concentration with residence time. Note the enlarged scale of the yield axes.

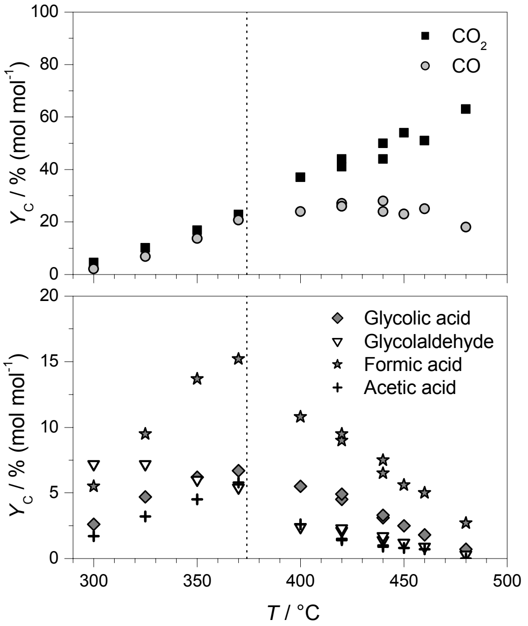

Figure 9: Product yields at 4 - 7 s, 24 MPa (T < 374 °C) / 34 MPa (T > 374 °C) and stoichiometric oxygen concentration with temperature. Dotted line: critical temperature 374 °C.

Carbon balance closure above 350 °C generally improves upon stoichiometric oxygen addition to 77 - 92 % and reactor effluents are less coloured. Therefore oxygen seems to inhibit humin formation to a certain extend.

Glucose decomposition kinetics could be described with a simple global first order rate expression (first order in respect to molar concentration of Glucose under reaction conditions). A pre-exponential factor of $1.3 \cdot 10^{11}$ s^{-1} and an activation energy of 130 kJ mol^{-1} were obtained by drawing an Arrhenius plot with calculated rate constants in the range from 250 to 370 °C in - for technical purposes acceptable - accordance with experimental data (see Figures 2, 3 and 7).

Higher temperatures were not considered since glucose conversion at supercritical temperatures is ≥ 99 % even at the lowest residence times. Nevertheless rate constants calculated by Arrhenius law could reproduce the high experimental conversions at supercritical temperatures.

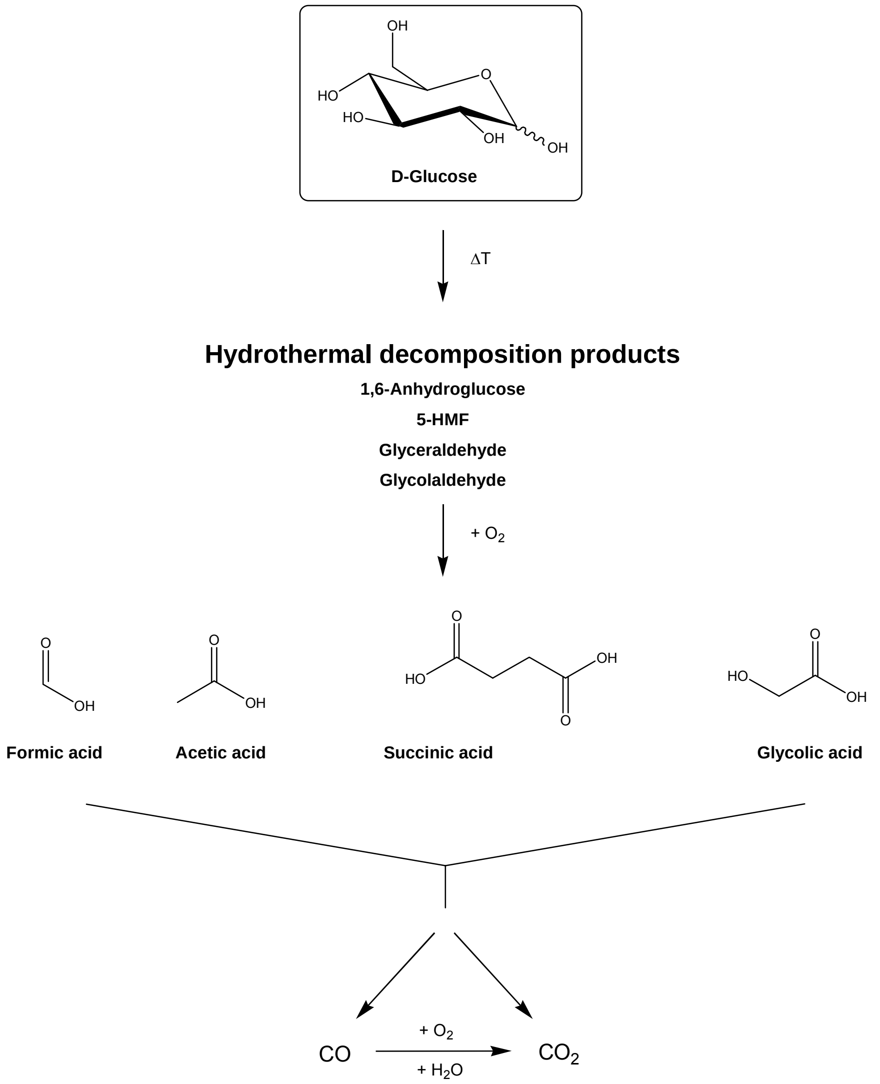

Figure 10: Reaction scheme for oxidative decomposition of glucose in sub- and supercritical water. Formed CO reacts slowly to CO_2 via direct oxidation and water gas shift reaction.

Discussion

A possible design for a total oxidation process for energy recovery from biomass is displayed in Figure 11. A mixture of biomass and water is brought to reaction pressure (25 MPa) by high pressure pumps and then heated up by hot reactor effluents. In the reactor at approx. 600 °C the organic matter reacts with oxygen, provided by compressed air. The reaction heat is used to generate process steam and to heat up the incoming feed stream in an eco heat-exchanger. Subsequently the reactor effluent is cooled further down to ambient temperature and decompressed to ambient pressure. Finally gas phase and liquid phase are separated. Both, gas stream and liquid stream are expected to meet German release standards AbwasserV and 17. BImSchV (Schmieder and Abeln 1999). Alternatively the oxygen needed for combustion could be provided as liquid oxygen, which is then brought to system pressure by a high pressure pump. Anyway economic evaluations point out the compression of air to be the measure of choice. The feed should at least carry an organic mass fraction of 0.5 % (g g^{-1}). In small scale plants (low feed stream or feed with high moisture and low energetic content) the generated process steam could be used directly for heating purposes. In larger plants (≥ 10 t h^{-1}) with relatively high feed concentration of organic substances > 3 - 7 % (g g^{-1}), a steam cycle can be employed to generate valuable electric power (Klingler 2001).

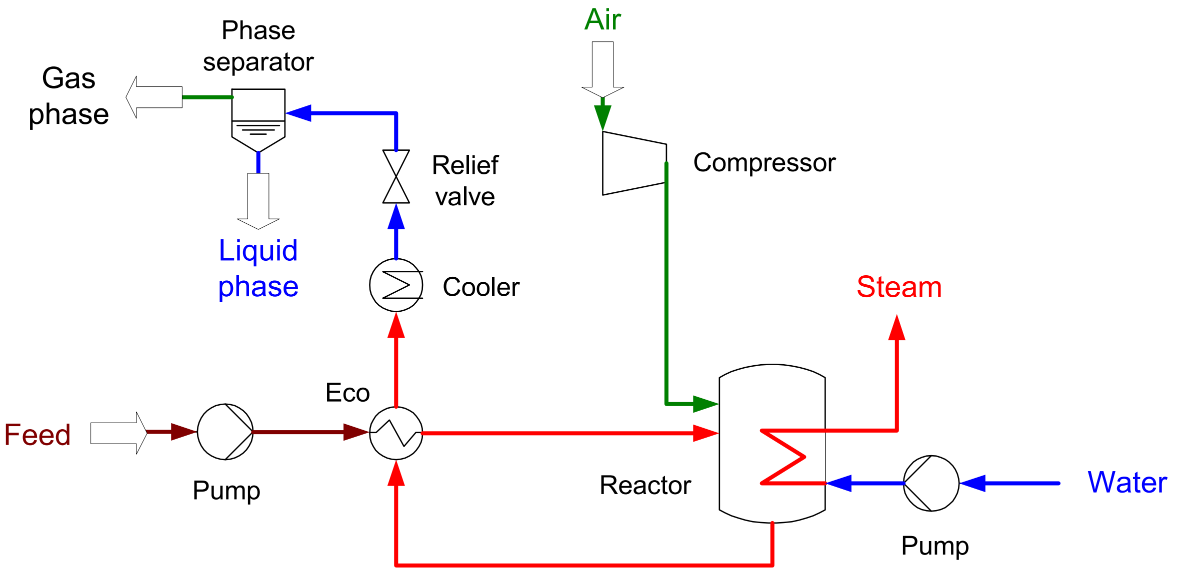

Figure 11: Flow sheet of a total oxidation process for biomass in supercritical water with oxygen supply by compression of air and steam generation.

Conclusions

A complete combustion of glucose in supercritical water to CO_2 and H_2O could not be achieved even at temperatures as high as 480 °C. Glucose decomposes already at sub-critical temperatures readily to low-molecular liquid substances, chiefly organic acids, but most of these are more stable and react only slowly with oxygen. In addition large amounts of unwanted CO (approx. 20 % (mol mol^{-1}) are produced. Complete combustion needs higher temperatures > 480 °C or longer residence times > 7 s. Nevertheless valuable insight in reaction products and mechanisms could be gained. The decomposition kinetics could be expressed by a global first order rate model with acceptable precision.

Feasibility evaluations point towards a process design with oxygen supply by compressed air as the most attractive alternative. The energetic content of biomass is used to generate steam, which in turn can be utilised for heating purposes or at larger scales for electric power generation.

Acknowledgements

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