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Technische Universität Hamburg-Harburg

TECHNICAL NOTE: 4.7

DETAILED CHARACTERISATION OF CARBON AND NITROGEN MASS BALANCES OF THE OPTIMISED SUB-CRITICAL LIQUEFACTION UNIT

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1 INTRODUCTION

This Technical Note covers the latest results of the hydrothermal treatment of wheat straw and lignin in sub- and nearcritical water. A detailed description of the planning and the current state of the preparation and assembly of a new reaction unit is given. It was agreed by contract to deliver this unit by the start of the third year of the prolongation phase to Partner 1.

Based on the results of the preceding Technical Notes it could be concluded that the non-oxidative treatment of ligno-cellulotic biomass does not result in a complete conversion to water-soluble and gaseous species. For such wastes, the treatment with carbon dioxide and the resulting decrease in pH did not result in complete liquefaction but left a significant portion of insoluble substances based on a carbon balance. This residual, very recalcitrant fraction can probably be attributed to lignin. Because of this conclusion preliminary experiments adding hydrogen peroxide as an oxidant were conducted. In these experiments the SCWO-technology (Supercritical Water Oxidation) was applied to lignin and wheat straw. The effluents obtained from the oxidative treatment were absolutely solid-free and had a dissolved organic carbon content corresponding to 10-20 % of the total influent carbon. These results indicated that the influent carbon, which mostly consists of water-insoluble compounds, can be completely converted to water-soluble substances and gaseous species in the course of the oxidative destruction.

The focus of the present Work Package was laid on the oxidative treatment employing hydrogen peroxide as the oxidizing reagent. Following the preliminary experiments with lignin and wheat straw, a systematic parameter study was conducted. The goal of this study was to characterize the influence of temperature and amount of hydrogen peroxide on the oxidative destruction of plant derived biomass. The experiments were analyzed by the liquid effluents, which were characterized with respect to the residual carbon content. Furthermore, it was attempted to identify and quantify main products of the hydrothermal oxidation of wheat straw and lignin.

2 MATERIALS AND METHODS

Experimental set-up:

The studies on the oxidative conversion of wheat straw and lignin were conducted in the continuous flow reactor illustrated below. The influent suspension is introduced into the system by means of a high pressure membrane pump and moderately preheated to avoid the onset of thermo-chemical decomposition before the reaction unit. Pure water is fed to the system by a separate line and heated to high temperatures upstream of the mixing point. By mixing the two streams in a mixing tee the temperature of the influent suspension can instantaneously be raised to the desired level, resulting in a controlled start of the reaction. The biomass is treated at isothermal conditions and cooled down immediately by a double-pipe heat exchanger coupled to the outlet of the tubular reaction unit. Figure 1 shows a schematic sketch of the experimental apparatus.

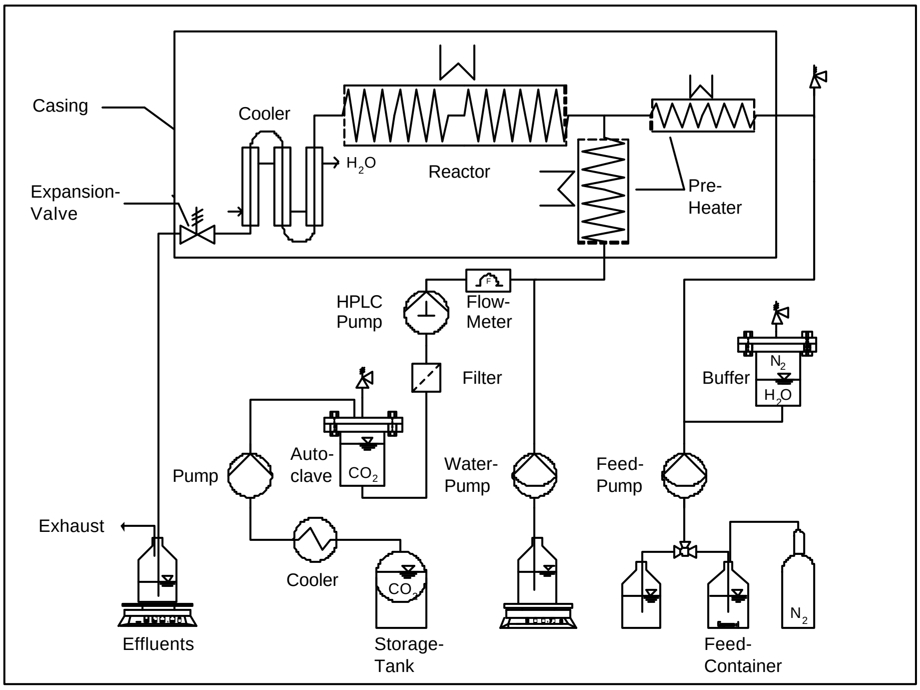


Figure 1: Schematic sketch of the experimental apparatus

The residence time within the reactor can be varied to a certain degree by adjusting the pump settings and by installing tubular reaction units of different length and corresponding internal volume. The third line delivering carbon dioxide to decrease the pH of the influents was not used in the studies presented in this Technical Note.
Hydrogen peroxide was introduced together with the biomass suspension. The amount of oxidant was calculated on the basis of the structural formula.

Materials:

The model compound studies on the hydrothermal degradation of ligno-cellulotic materials were done with pure alkali lignin (Sigma-Aldrich). The wheat straw was provided by a local farmer.

In the studies on the oxidative treatment of biomass hydrogen peroxide (Sigma-Aldrich) was applied as the oxidizing reagent and was used as received.

Analytical methods:

The amount of liquefied organic compounds was determined by measuring the dissolved organic carbon content in a DOC analyser (Analytik Jena „multi N/C 3000“) as a lumped parameter to characterize the degree of conversion to water-soluble substances.

The reaction effluents were analysed for carboxylic acids with the GC system of Partner 3. This system consists of a gas chromatograph (Varian 3900) equipped with a capillary column (WCOT fused silica) and a flame ionisation detector operated at 220°C. The samples are acidified by 2 % phosphoric acid prior to injection. For each run a sample volume of 0.5 µl was injected using nitrogen as carrier gas. The temperature program is as follows: After an initial holding time of 1 min at 60°C the oven temperature is increased by a rate of 10°C/min to the final temperature of 200°C. By this method carboxylic acids higher than formic acid can be detected and quantified. Formic acid cannot be detected by FID but would require alternative methods like HPLC for detection.

In addition to the quantification of carboxylic acids, GC-MS analyses were conducted on selected samples for the characterization of further, unknown degradation products. These analyses were conducted in the Central Analytical Laboratory of the Technische Universität Hamburg-Harburg.

The system used for the analyses was a HP5890 gas chromatograph with a HP5971A MS engine. The ionisation was accomplished by EI (70eV). A two-step temperature program was applied for separating the reaction products on a capillary column (DB-5ms): Starting temperature: 70°C (2 min) with a subsequent heating rate of 5°C/min to 170°C and a following heating rate of 10°C/min to 290°C and a final holding time of 10-15 min at 290°C. An aqueous sample of 4 ml was extracted with an equivalent volume of dichloromethane.

3 RESULTS AND DISCUSSION

Based on the preliminary experiments, the studies on the oxidative treatment of plant derived biomass were continued during the current Work Package. For these studies, alkali lignin was investigated as a model compound for ligno-cellulotic biomass. Wheat straw was studied as a real biomass waste and an ingredient of the substrate specified by ESA. The aim of this work was the optimization of the operating conditions in terms of a complete degradation of solids as well as the identification of main soluble reaction products.

3.1 Oxidative destruction of lignin

The results obtained so far revealed that lignin-containing wastes like wheat straw cannot be completely converted by hydrolysis at the conditions applied. In addition, the hydrolytic treatment of pure lignin leads to the formation of carbon-rich, solid residues which eventually caused plugging of the flow reactor. The current studies were therefore focussed on the oxidative destruction of plant biomass in sub- and nearcritical water by varying the amount of hydrogen peroxide and the operating temperature. The mean residence time could not be systematically varied due to the limited volume of the continuous flow reactor and the low fluid density at elevated temperatures.

The degree of conversion of pure lignin to gaseous products is shown in Figure 2.

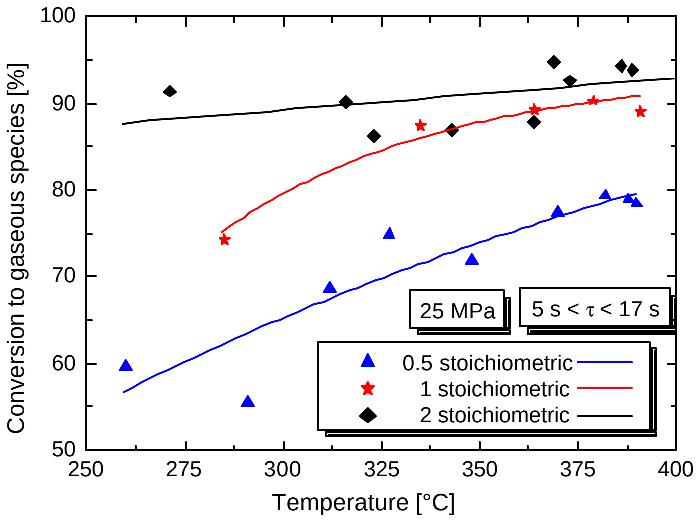


Figure 2: Lignin conversion to gaseous species on a carbon balance, influence of amount of oxidant and temperature

The conversion to gaseous species was calculated on the basis of the aqueous phase analysis. This approach was feasible since no solid residues possibly contributing to the carbon balance were observed in the effluents. Providing at least half the stoichiometric demand yielded solid-free effluents at the temperatures applied.

The conversion to gaseous species increases with increasing temperature at hydrogen peroxide concentrations corresponding to half the stoichiometric and the stoichiometric demand. Supplying twice the stoichiometric amount yields only a very minor increase of gaseous products with increasing temperature. The portion of gaseous products is essentially constant and contributes to about 90-95 % of the total influent carbon, meaning that the residual DOC is about 5-10 % of the influent carbon at overstoichiometric hydrogen peroxide supply.

It can be concluded that the stoichiometric and overstoichiometric oxidant supply lead to a nearly complete oxidation of lignin in less than 20 s. About 10 % of the influent carbon remains in the liquid effluents as DOC at temperatures up to 390°C. In order to identify these refractory compounds samples of the liquid effluents were subjected to the GC methods described above.

Acetic acid is known to be a relatively stable intermediate in the total oxidation of organic wastes in water at elevated temperatures and pressures. The amount of carbon bound as acetic acid with respect to the total dissolved carbon in the liquid effluents is depicted in Figure 3.

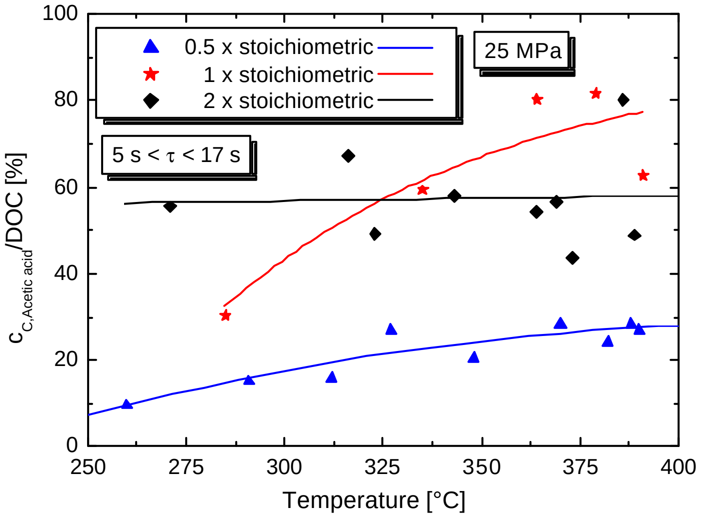


Figure 3: Oxidative conversion of lignin, portion of carbon bound as acetic acid to total organic carbon

The results show that acetic acid constitutes the main degradation product providing the stoichiometric demand and an overstoichiometric amount of hydrogen peroxide, respectively. At stoichiometric supply, acetic acid contributes to up to 80 % of the dissolved carbon at nearcritical conditions, while at overstoichiometric conditions acetic acid amounts to about 50-60 % on average. These values are, however, subject to larger deviations due to the almost complete oxidation and the low absolute concentrations of dissolved organic carbon. In contrast, the partial oxidation providing half the stoichiometric demand results in much lower acetic acid concentrations, contributing to 20-30 % of the dissolved carbon at nearcritical conditions. This is probably due to the formation of partial oxidation products, which are not as highly oxidized as acetic acid.

Carboxylic acids higher than acetic acid have a comparatively minor contribution to the dissolved carbon.

Samples of the oxidative treatment of lignin were further analyzed by GC-MS in the Central Analytical Laboratory of the Technische Universität Hamburg-Harburg. In case of the stoichiometric and overstoichiometric oxidant supply, no further degradation products could be

detected in quantifiable amounts due to the very low residual dissolved carbon content. For the partial oxidation supplying half the stoichiometric demand, compounds other than carboxylic acids could be identified. The partial oxidation products identified were mainly phenol, benzoic acid, benzaldehyde and derivatives thereof, as well as alkylbenzenes.
In total, about 30 % of the total dissolved carbon could be identified in case of partial oxidation. The remaining carbon can probably be attributed to formic acid and other short-chain polar substances, which could not be detected by GC-MS due to the liquid/liquid extraction step with toluene and dichloromethane, respectively.

Summing up these aspects, the nearcritical water oxidation can be regarded as a very efficient means to convert lignin to soluble and gaseous substances. In case of stoichiometric oxidant supply, lignin can be readily converted to gaseous species, leaving only about 10 % of the total influent carbon in the aqueous phase. In addition, a high selectivity for the formation of acetic acid, being in the range of 80 % at nearcritical conditions, was observed.

3.2 Oxidative treatment of wheat straw

Following the experimental study on lignin conversion under oxidative conditions, wheat straw was subjected to hydrothermal treatment in sub- and nearcritical water. This study was aimed at the question, whether the results of the model compound studies can be transferred to a real, insoluble bio-waste. In accordance with the lignin study, wheat straw was treated both by partial oxidation, providing half the stoichiometric demand, as well as by total oxidation, supplying twice the stoichiometric amount of hydrogen peroxide. In addition, experiments under hydrolytic conditions, without adding any oxidant, were conducted to compare both processes in terms of residual carbon content and main degradation products.

The effluents were characterized in terms of the ratio of dissolved carbon to the total influent carbon and the contribution of carboxylic acids to the solubles. The effluent DOC was measured directly, while the influent carbon was calculated on the basis of the elementary analysis of the input material.

The results of the wheat straw experiments in terms of the residual dissolved carbon content are depicted in Figure 4.

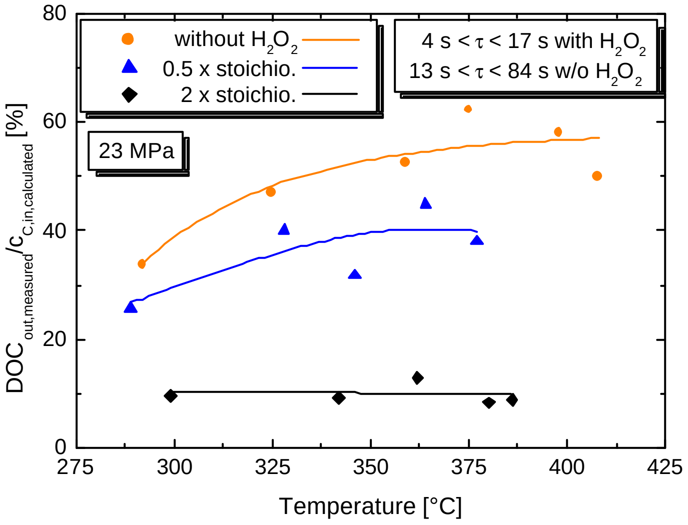


Figure 4: Conversion of wheat straw to water-soluble substances, influence of amount of oxidant and temperature

It can be inferred that the degree of liquefaction under non-oxidative conditions increases with temperature up to 60 % in the nearcritical region. These results are in line with past experiments on the non-oxidative destruction of wheat straw, which yielded a maximum degree of liquefaction of about 70-80 % under optimized conditions. The effluents of all of the non-oxidative runs still contain solids. A marked gas evolution could not be observed. Thus, it can be concluded that about 40 % of the influent carbon is still present as insoluble carbon after non-oxidative treatment.

In contrast, the oxidative destruction of wheat straw returns essentially solid-free effluents. Except of the run with half the stoichiometric amount of hydrogen peroxide at a temperature below 300°C, all effluents were solid-free. In case of the partial oxidation, about 35-40 % of the total influent carbon were liquefied, meaning that the remaining portion was converted to gaseous species.
Supplying twice the stoichiometric demand results in a residual dissolved carbon content of about 10 %, essentially independent of the temperature applied. As in case of pure lignin,

about 90 % of the influent carbon were transformed into gaseous substances within residence times of less than 20 s.

The results of the acetic acid analyses are shown in Figure 5.

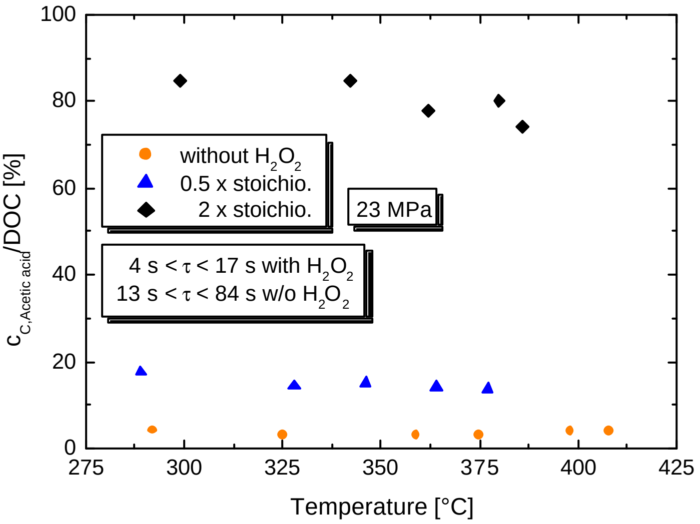


Figure 5: Wheat straw conversion, portion of carbon bound as acetic acid to total organic carbon

Acetic acid has a very minor contribution to the dissolved organic carbon at non-oxidative conditions, roughly amounting to 5 % of the total dissolved carbon. In contrast, supplying half the stoichiometric amount leads to an increase in acetic acid concentration to 15-20 %. This portion seems to be independent of temperature over a wide range from well-subcritical to nearcritical conditions. Increasing the amount of oxidant to twice the stoichiometric demand leads to the selective formation of acetic acid, which is produced with a selectivity of about 80 %.

In accordance with the studies on pure lignin, acetic acid is a relatively stable intermediate in the total oxidation of wheat straw. In order to completely eliminate any residual DOC in the effluents, the operating range would have to be adjusted to higher temperatures and residence times. However, the complete conversion to gaseous products is beyond the scope of the project. The selective formation of acetic acid by providing excess oxidant appears to be an attractive alternative to complete gasification.

4 CURRENT STATE OF THE NEW APPARATUS

The delivery of a continuous flow through type apparatus for the hydrothermal treatment of biomass is a deliverable of hardware agreed by contract. The delivery date set is the beginning of the third year of the project, August 2005. The design of the apparatus is similar to the existing one operated in the Department of Thermal Process Engineering. The main specifications are summarized below.

- Maximum pressure: 300 bar
- Maximum temperature: 400°C
- Throughput: 5 kg/h
- Initial solid concentration: 1-2 wt-%
- Reaction volume: ~ 100 ml

It was further agreed to design the apparatus as a transportable unit, meaning that all peripheral equipment like pumps and control units have to be placed in one mobile frame. The apparatus is further capable of delivering carbon dioxide and it is designed to withstand corrosive environments as in the case of using hydrogen peroxide for the oxidative treatment of biomass.

The apparatus consists of three separate lines upstream of the reactor: One line (line 1) delivers the biomass suspension (along with hydrogen peroxide). The second one (line 2) supplies pure, hot water to the systems. These lines are brought together upstream of the tubular reactor to instantaneously start the reaction. The third line (line 3) delivers liquid carbon dioxide to the system. It is connected to line 2 upstream of the pre-heaters.

The core of the transportable unit is the tubular reactor. The effluents are cooled down in a subsequent double-pipe heat exchanger and expanded to ambient pressure by a backpressure regulator.

The choice of a tubular reactor was discussed and agreed on at the last Progress Meeting in Paris. It was stated that in order to further increase operating temperature and residence time, as would be applicable for completely destroying PCBs, a different set-up using an autoclave would be the preferred choice. However, this possible alternative was discussed but not intended to be implemented in the new apparatus.

A detailed description of the main parts is given in the following.
A complete documentation of the overall set-up including detailed manuals and information on the main parts will be submitted along with the apparatus. The preliminary design discussed here is illustrated in the flow scheme above (see figure 1).

Line 1, biomass delivery:

The first line consists of a high pressure metering pump (LEWA, EK1) and the feed pre-heater. The metering pump is designed as a membrane pump to allow the processing of solid particulates up to an operating pressure of 300 bar. The discharge flow can be varied manually by adjusting the stroke length of the pump operating at constant rotational frequency. The pump is available at Partner 4. The pre-heater consists of a high pressure pipe (O.D.: 1/4 inch, L: 6 m) which is spirally wound to fit in a heating jacket (1.5 kW). The heating jacket is a resistance heater with a ceramic contact area designed for a maximum temperature of 500°C. The surface temperature is measured by a thermocouple (specified below) between the heating jacket and the high pressure pipe.

Line 2, hot water line:

The second line delivering high temperature water serves the purpose of rapidly heating-up the feed suspension. It consists of a metering pump (LEWA, EK1, available at Partner 4) and two 1.5 kW heating jackets.

Line 3, carbon dioxide delivery:

The third line is made of the CO_2-storage cylinder (not included in the deliverable), a cooling unit with an integrated air driven pump, a storage vessel, a metering pump, and a flow meter. The integrated cooling and pump unit (Pickel-Modul) liquefies and pressurizes the carbon dioxide and delivers it to the storage vessel. The exact amount of carbon dioxide is delivered from the storage vessel by means of a HPLC-pump. The mass flow meter (Rheonik) measures and indicates the actual mass flow of carbon dioxide.

Reaction unit:

The tubular reactor is made of two sections of high pressure pipe (O.D.: 1/4 inch, L: 2 x 6 m, internal volume 90 ml). Each section is placed in a 1.5 kW heating jacket to compensate heat losses and achieve the maximum outlet temperature.

High pressure pipe:

All high pressure piping subjected to high temperature environment is made of corrosion resistant material (Alloy 600). All high pressure / high temperature fittings connecting the ¼" piping are purchased from Swagelok and made of the same material.

Double-pipe heat exchanger:

The double-pipe heat exchanger is made of the inner high pressure pipe and an outer stainless steel tube. It consists of 4 sections, each section having a length of 70 cm. The effluents are cooled by tap water flowing in the angular gap between the inner and the outer pipe.

Backpressure regulator:

The system pressure is manually adjusted by a spring-loaded backpressure regulator (Tescom Europe). The past experiments on the conversion of biomass have shown that such equipment could be reliably operated with cellulose and wheat straw. However, the non-oxidative treatment of real biomass samples received in the frame of the closed loop experiments led to problems due to attrition of the seat of the backpressure regulator. It is therefore planned to introduce a gravity separator upstream of the regulator valve when treating the materials obtained from the bioreactors at non-oxidative conditions. By providing an increased cross-sectional area the flow velocity decreases and coarse particles are allowed to settle. It is intended to use a 1 litre separator with an inner diameter of 70 mm to remove particles larger than 50 µm before entering the regulator. The solids can be withdrawn from the separator by a combination of two ball valves at the bottom of the vessel.

Control unit / data logging:

The control unit and data logging system was designed by the Electronic Laboratory of the Technische Universität Hamburg-Harburg. The complete system is housed in a 19 inch rack (Ratiopac). The control unit consists of five temperature controllers (Eurotherm 2132), each of them controlling one alternating current plug socket for one heating jacket by a solid state relay. The input signals of the controllers are delivered by 5 thermocouples placed under the heating jackets.

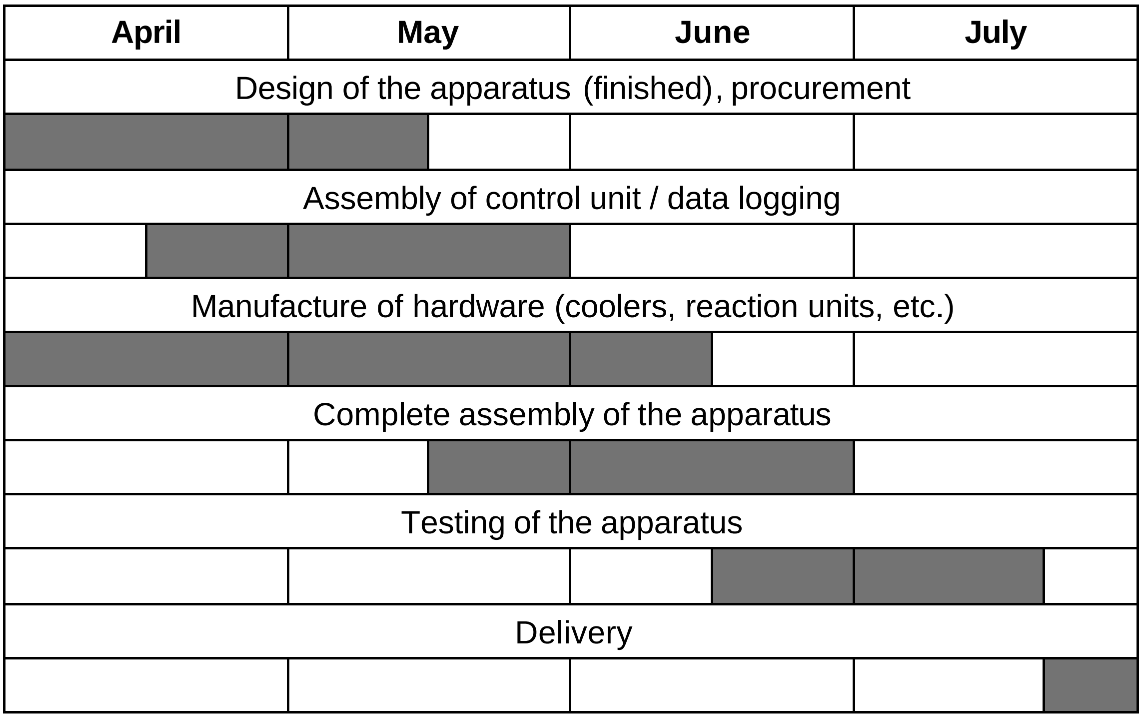
The data logging systems consists of two 8 channel bus modules and one signal converter. It is planned to measure the system temperature at 5 different locations by thermocouples and the system pressure at one single point by a pressure transducer. The system temperature will be measured downstream the pre-heaters, at the inlet as well as the outlet of the reactor and at the outlet of the double-pipe heat exchanger. All temperature and pressure signals are transferred to a personal computer by its serial interface and are displayed and recorded by software developed at the Electronic Laboratory.

The thermocouples are type K (NiCr-Ni) with a jacket made of Alloy 600. The thermocouples measuring the temperature within the apparatus will be introduced into the system by tee-connectors.

Current state:

The design of the new unit is completed. All parts necessary for assembling the apparatus have been ordered in the meantime. However, it might take until the middle of May before the last parts will arrive. This might be the case for the heating jackets, the backpressure regulator, and the high pressure pipe. In the meantime, the manufacture and assembly of hardware will proceed. It is envisaged to have the unit completed by the end of June to have sufficient time to run tests and to deliver the apparatus to Partner 1 at Ghent.

The schedule of the tasks before delivery is illustrated by the bar chart in Figure 6.



	April		May		June		July	
Design of the apparatus (finished), procurement	▨	▨	▨					
Assembly of control unit / data logging		▨	▨	▨				
Manufacture of hardware (coolers, reaction units, etc.)	▨	▨	▨	▨	▨			
Complete assembly of the apparatus				▨	▨	▨		
Testing of the apparatus						▨	▨	
Delivery								▨

Figure 6: Bar chart illustrating the time schedule of the tasks before delivery

5 CONCLUSIONS / OUTLOOK

According to the work package descriptions experimental studies on the conversion of pure lignin and wheat straw have been performed. The experimental results show that nearcritical water oxidation technology can be successfully applied to destroy ligno-cellulotic biomass within residence times in the order of seconds. By supplying an excess of hydrogen peroxide the solid matter can be completely converted to water-soluble substances and gaseous species with a high selectivity of acetic acid formation. In addition, closed-loop experiments with solid residues of Partner 1 have been conducted and effluents of the hydrothermal treatment have been distributed to Partner 1 to close the loop.

The planning of the new reaction unit to be delivered to Partner 1 has been completed and the manufacture and assembly was started. It is intended to have the assembly completed by end of June to test the equipment and to deliver the hardware on time.