MELiSSA

TECHNICAL NOTE

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Technische Universität Hamburg-Harburg

TECHNICAL NOTE: 4.5

TESTING OF ADDITIONAL LIQUEFACTION TECHNOLOGIES WITH RAW (MODEL) SUBSTRATE

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1 INTRODUCTION 11~~0~~

2 MATERIALS AND METHODS 12~~0~~

3 RESULTS AND DISCUSSION 4
- 3.1 Liquefaction of pure Cellulose 4
- 3.2 Wheat Straw Degradation 114~~0~~
- 3.3 Lignin Degradation 134~~0~~

4 CONCLUSIONS / OUTLOOK 154~~15~~

TABLE OF CONTENTS

1 INTRODUCTION

Based on the results of the 1st project phase it was agreed on that additional conversion technologies, namely the acidification by carbon dioxide and the oxidation by means of a proper oxidant, were to be evaluated. The application of the former technology has shown promising results in the liquefaction of pure cellulose in subcritical water. It was therefore intended to investigate the influence of carbon dioxide addition by a systematic parameter study and to compare the results in terms of conversion to water-soluble substances for pure water and the system water/carbon dioxide. In addition, this approach was applied in the liquefaction of wheat straw as the possibly most persistent ingredient of the MELiSSA substrate.

Since the treatment of the raw substrate and the residues of Partner 1 resulted in an incomplete liquefaction, it was assumed that the fraction of the ligno-cellulotic material which can be attributed to lignin cannot be totally converted by hydrothermolysis. It was therefore planned to employ SCWO-technology (Super critical Water Oxidation) in order to convert the residual portion of solid particulates. Due to the corrosive environment in SCWO-processes, all pressure bearing parts of the apparatus which are subjected to high temperatures had to be replaced by highly corrosion resistant construction materials (Inconel 600, Inconel 625). These tasks, along with the implementation of a high temperature oven for extending the operating range to temperatures well above the critical point of water, were completed in preparation for the oxidation experiments. Lignin (organosolv lignin, alkali lignin) was chosen as a model substrate for the preliminary tests using hydrogen peroxide as the oxidant. Also, a set of experiments subjecting wheat straw to an oxidative treatment in near-critical water was conducted.

2 MATERIALS AND METHODS

The materials, the experimental procedure, and the analytical methods have been described in detail in the preceding Technical Notes. Since the beginning of the prolongation phase several modifications have been done to the experimental set-up in order to extend the reaction time and the temperature range and to conduct experiments at SCWO-conditions. Figure 1~~Figure~~ 1Figure 1 shows a schematic sketch of the experimental apparatus.

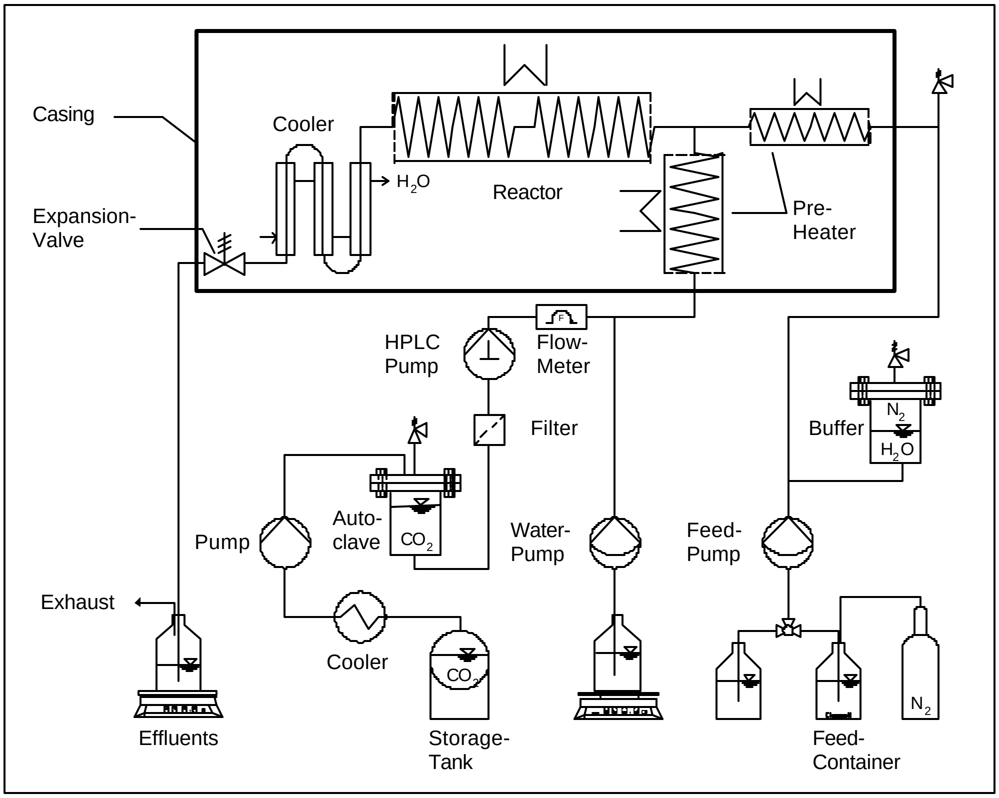

Figure 1: Schematic sketch of the experimental apparatus

A ball valve was connected to the outlet of the double pipe heat exchanger (cooler). The aim of this modification was to significantly increase the reaction time within the reactor by rapidly closing the ball valve and shutting down the pumps simultaneously. By this semi-continuous operating mode it was intended to obtain data points and to validate the model for the reaction kinetics at reaction times which cannot be accomplished by means of a flow reactor in fully-continuous mode due to the restrictions in reactor geometry.

During the first project phase experiments were mainly conducted at subcritical to near-critical water conditions. Aiming at the destruction of persistent substances by supercritical water oxidation a high temperature oven (4kW) with an additional 6 m of high pressure piping (1/4”) was integrated into the set-up. This modification allows operating temperatures up to 500°C, which is well above the critical temperature of water (374°C). The oven can either be connected to the reaction coils, which are powered by heating jackets, to further extend the residence time or it can be operated directly downstream the mixing point.

Due to the possibly corrosive environment at SCWO-conditions all piping downstream the mixing point was replaced by highly corrosion resistant material (Inconel 600).

In some experiments, the reaction coils were replaced by a fixed bed assembly as an alternative means to extend the residence time of solid particulates within the reaction zone, assuming that that the treated material did not dissolve in water at operating conditions. The principle of this set-up is illustrated in Figure 2~~Figure 2~~Figure 2.

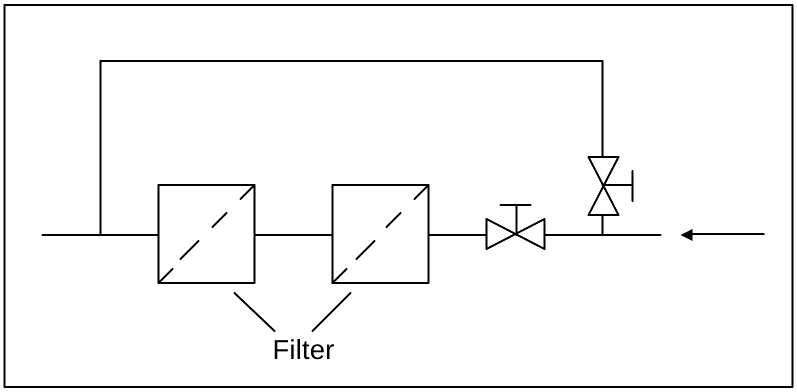

Figure 2~~2~~2: Fixed bed assembly for the treatment of biopolymers

The fixed bed is made of two T-filter units which are coupled by a piece of high pressure piping. The solid material, namely wheat straw and organosolv lignin, is filled in the sinter metal inlet of the upstream unit and is contained between the filters during the experiment. In order to minimize the time for heating up the assembly to operating temperatures a bypass was added to the system. During the heating up period the pure water was processed through the ~~p~~bypass to avoid the onset of any reactions within the fixed bed. Once the desired temperature was reached, the valves were switched and the water stream was allowed to flow through the fixed bed containing the biomass for a preset time period. Due to the significant heat capacity of the body of the high temperature valve (Sitec) and the filter units, a marked temperature fall could be observed during the first minutes , followed by a temperature increase to the desired level.

3 RESULTS AND DISCUSSION

3.1 Liquefaction of pure Cellulose

The systematic study of the liquefaction of pure cellulose in subcritical water has been continued in the prolongation phase for two reasons. Firstly, cellulose is the most abundant biopolymer in the world and the most important constituent of plant derived biomass. Cellulose accounts for the main part of the fibre fraction of the ESA-substrate, so that it can be considered as a proper model compound for the conversion of plant biomass in the ESA-substrate. Secondly, cellulose was employed to elucidate the feasibility of enhancing the conversion to water-soluble products by adding carbon dioxide. By this means the pH can be lowered and acid catalysed reactions will presumably proceed at faster reaction rates.

At the end of the first project phase, detailed data sets for the liquefaction of cellulose at 250 bar and temperatures of 250°C, 270°C, 290°C, and 310°C had been available. In addition, experiments adding carbon dioxide had been conducted at temperatures from 250°C to 290°C. The comparison of the respective degrees of liquefaction for pure water and the system water/carbon dioxide revealed a marked increase in reaction rate for the catalysed system at a temperature of 250°C. It was therefore decided to complete and refine the parameter study in the temperature range from 240°C to 280°C.
All experiments were done with an initial cellulose concentration of 0.5 wt-% in the feed suspension, which results in a cellulose concentration of 0.1-0.5 wt-% at the reactor inlet, depending on the mass flow ratios of feed and pure water flux. For this diluted system the reaction kinetics were assumed to be independent of the solid concentration and the evaluation in terms of residence time was performed using the properties of pure water.
Figure 3~~Figure 3Figure 3~~ shows the degree of liquefaction f calculated on a carbon basis (DOC_{out}/TC_{in}) for the temperature range from 250°C to 310°C.

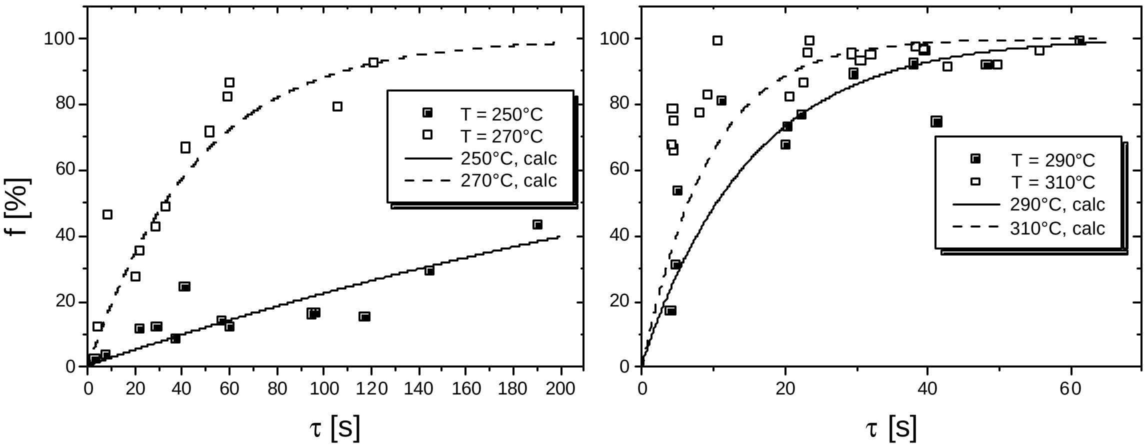

Figure 3~~33~~: Degree of liquefaction for pure cellulose in water, T: 250°C – 310°C, P = 250 bar

It can be inferred that the rate of reaction increases with increasing temperature. While at a temperature of 250°C only about 40 % of the cellulose are converted to water-soluble substances after 3 minutes, the conversion can be regarded as being complete at a temperature of 310°C within less than half a minute. The corresponding curves depicted in the figure were calculated by modelling the reaction kinetics with a first order approach.

Additional experiments were conducted at temperatures of 240°C, 260°C, and 280°C for an accurate determination of the kinetic parameters in the subcritical region. The results of these experiments are depicted in Figure 4~~Figure 4~~~~Figure 4~~.

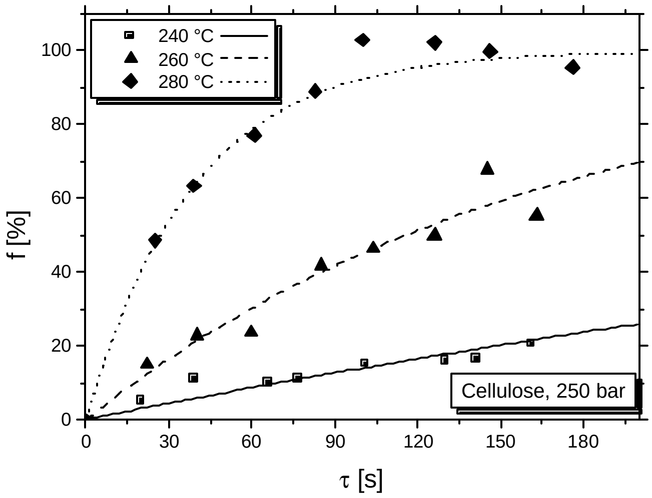

Figure 444: Degree of liquefaction for pure cellulose in water, T: 240°C , 260°C, 280°C, P = 250 bar

The additional data are in good agreement with the results of the previous experiments, which proves the plausibility of the results. Also, selected experiments have been done in duplicate and triplicate to gain information about the reproducibility of the experiments. Based on the results of this check the mean deviation can be estimated to be in the range of 5 %.

As mentioned above, the curves illustrated in the figures have been calculated by modelling the conversion with a first order approach. For such an approach the degree of conversion in a tubular reactor can be written as follows:

$$f = 1 - \exp(-k \cdot t) \qquad \text{(equation 1)}$$

and after rearrangement:

$$\ln(1 - f) = -k \cdot t \qquad \text{(equation 2)}$$

where k denotes the reaction rate constant.

In case the rate of conversion can accurately be described by a first order kinetic, the reaction rate constant can be read as the slope of a ln(1-f) versus τ diagram. Such a diagram is depicted in Figure 5~~Figure 5~~~~Figure 5~~ for the temperature range from 240°C to 310°C.

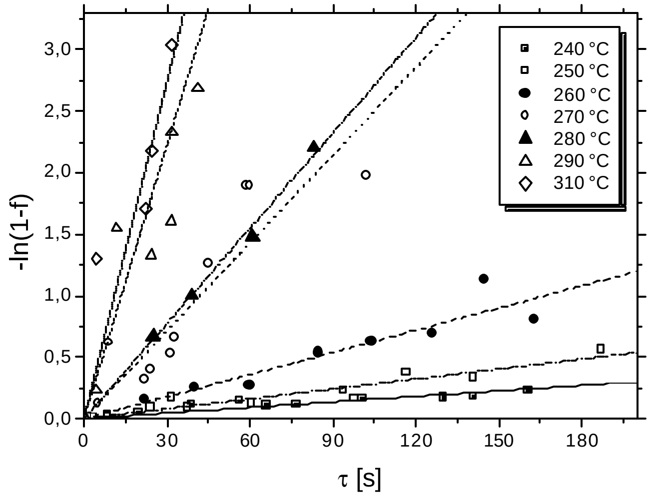

Figure 5~~5~~~~5~~: Determination of the reaction rate constant from the respective conversion data

It can be concluded that the data are reasonably well reflected by a linear regression, which in turn means that the description of the reaction kinetics by a first order approach is applicable. This is especially valid for lower temperatures, where the data very accurately obey a linear relationship.

The reaction rate constants at different temperatures can be determined by reading the values of the slope of the straight lines. These values are given in Table 1~~Table 1~~~~Table 1~~.

T [°C]	240	250	260	270	280	290	310
k(T) [1/s]	0.0015	0.0025	0.0062	0.0214	0.0263	0.0647	0.1086

Table 1: Reaction rate constants at different temperatures

A common approach to express the temperature dependence of the reaction rate constant is the Arrhenius' law:

$$k_{C,A} = k_{0,C,A} \cdot \exp(-\frac{E_{C,A}}{R \cdot T}) \qquad \text{(equation 3)}$$

with k_0 being the pre-exponential factor and E the activation energy of the reaction.

Accordingly, these values can be obtained by plotting ln(k(T)) versus the reciprocal temperature and reading the ordinate intercept and the slope of the line. The Arrhenius' plot with the respective values of the pre-exponential factor and the activation energy is given in Figure 6~~Figure 6Figure 6~~.

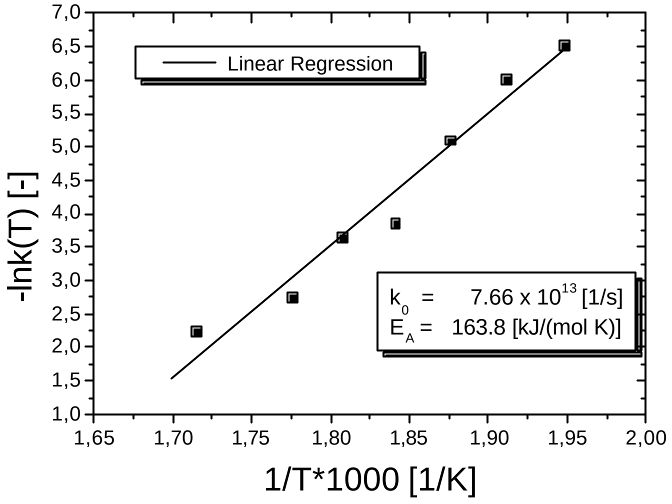

Figure 6~~66~~: Determination of kinetic parameters from the Arrhenius' approach

Summing up the results of this parameter study it can be concluded that the kinetics of the cellulose conversion in subcritical water can accurately be described by the equations stated above. In the temperature range investigated in this study the influence of pressure is negligible due to the very minor pressure dependence of the fluid density.

Influence of carbon dioxide addition

During the last stage of the first project phase very promising results could be obtained by adding carbon dioxide to the influent suspension. The resulting drop in pH led to a marked increase in the rate of liquefaction at 250°C, while the amount of carbon dioxide addition with respect to the degree of saturation at given operating conditions exhibited a very minor influence. On the basis of these findings additional experiments were scheduled with carbon dioxide concentrations of 60-100 % with respect to saturation. The results of these experiments are summarized in Figure 7~~Figure 7Figure 7~~ together with the data for pure water.

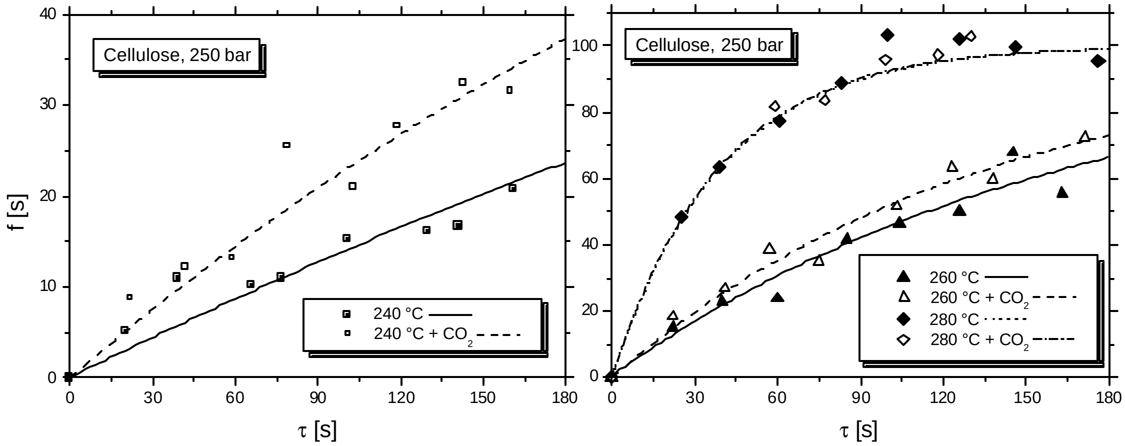

Figure 7~~7~~~~7~~: Cellulose conversion in water, water/carbon dioxide; T = 240°C (left);T = 260°C, 280°C (right)

The results reveal a catalyzing effect of carbon dioxide, which diminishes with increasing temperature. While at a temperature of 240°C the decrease in pH due to the addition of carbon dioxide clearly promotes the liquefaction of cellulose, this effect is less pronounced at 260°C and totally vanished at temperatures higher than 280°C. These findings are in line with the results of previous experimental runs, for which no enhancement in degradation could be observed at temperatures higher than 270°C.

Figure 8~~Figure 8~~~~Figure 8~~ depicts the reaction rate constants in the temperature range of 240°C to 260°C for pure water and water/carbon dioxide mixtures.

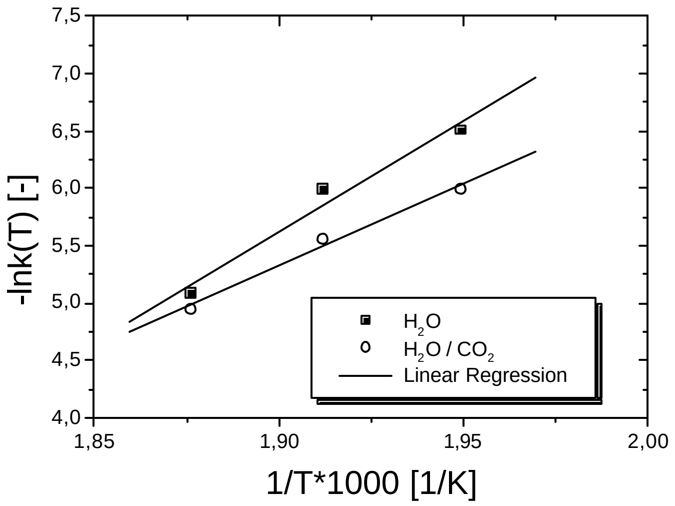

Figure 8~~8~~~~8~~: Arrhenius' plot for water and water/carbon dioxide mixtures

The lines in the Arrhenius' plot approach one another with increasing temperature, so that in case of cellulose no further enhancement in the rate of liquefaction can be obtained by adding carbon dioxide at temperatures higher than 270°C. Nevertheless, this method was applied at temperatures above 300°C for the degradation of wheat straw, since it was known from previous experiments that wheat straw is not as readily degradable as pure cellulose and might therefore be degraded at higher reaction rates in mixtures of water and carbon dioxide.

Product formation

The parameter study proves that cellulose can be converted to water-soluble products at high space-time-yields. The effluents of the thermal treatment in subcritical water were subjected to HPLC analyses in order to determine the amounts of sugars formed in the course of the reaction. The quantitative analysis shows that glucose as well as hydroxymethylfurfural (HMF) and pyruvaldehyd as secondary reaction products are formed in significant amounts during the hydrothermolysis of cellulose. The yields of these products are exemplified in Figure 9~~Figure 9Figure 9~~ for a temperature of 280°C.

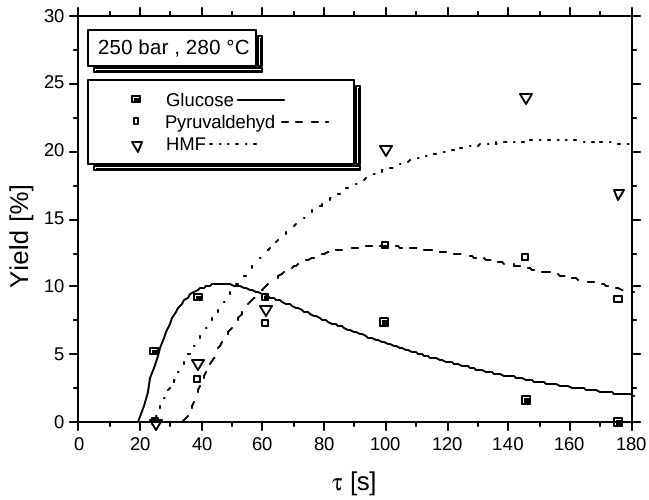

Figure 99~~9~~: Yield of main degradation products; T = 280°C, p = 250 bar

It can be inferred that glucose is not stable at the conditions applied in the experiments. As an intermediate product it is therefore subject to consecutive decomposition reactions according to the following scheme:

$$\text{Cellulose} \xrightarrow{k_1} \text{Glucose} \xrightarrow{k_2} \text{Secondary Products}$$

The curves depicted in the figure were derived by fitting the kinetic constants of the formation and the decomposition reaction to the experimental data. The parameters at other temperatures were determined similarly, so that the selectivity for the different degradation products can be expressed as the ratio of the yield to the respective degree of conversion. The selectivity of the glucose formation is depicted in Figure 10~~Figure 10~~~~Figure 10~~.

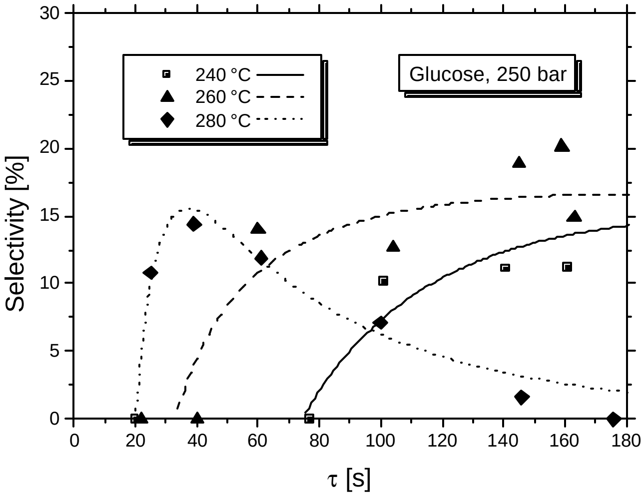

Figure 10~~10~~10: Selectivity of glucose formation; T = 240°C-260°C

The results evidence that the rate of glucose formation as well as glucose decomposition increase with increasing temperature, so that the maximum in selectivity is shifted to shorter reaction times with increasing temperature. Similar curves can be obtained for HMF and pyruvaldehyd, for which the maximum in selectivity occurs at longer reaction times and a higher level as compared to glucose.

The catalytic effect of carbon dioxide is also reflected by the course of the glucose yields. The decrease in pH associated with the addition of carbon dioxide leads to a marked increase in glucose yield due to the fact that the hydrolytic cleavage of the glycosidic bonds is an acid/base-catalyzed reaction. Again, the influence of carbon dioxide diminishes with increasing temperature as can be inferred by the course of the glucose yields depicted in Figure 11Figure 11Figure 11.

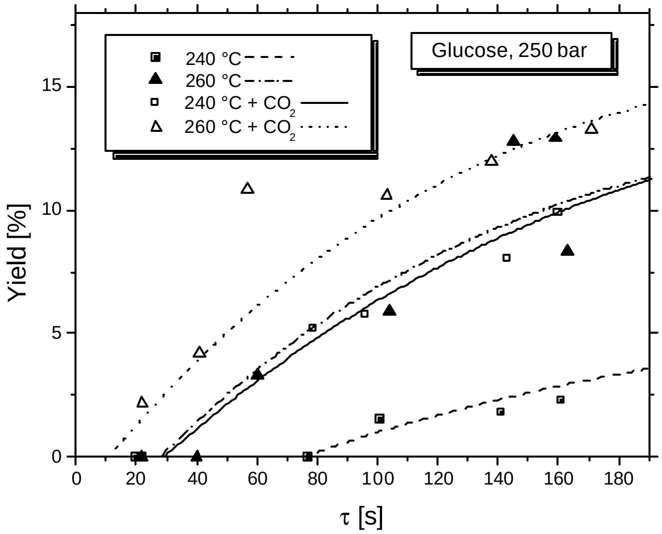

Figure 11~~11~~~~11~~: Glucose yields in water, water/carbon dioxide; T = 240°C, 260°C; P = 250 bar

3.2 *Wheat Straw Degradation*

Due to its significant amount of lignin and its ligno-cellulotic structure, wheat straw is the probably most persistent ingredient of the ESA-substrate. Wheat straw was therefore employed as a real waste in the investigation of the addition liquefaction technologies. Experiments were carried out over a wide temperature range from subcritical to supercritical conditions with and without adding carbon dioxide as a catalyst. Also, some preliminary tests have been performed with regard to the oxidation in supercritical water (see 3.3).
Experiments were mostly carried out in fully-continuous mode. Additionally, some experiments were conducted in fixed bed mode in order to increase the reaction time of water-insoluble solids by retaining them in the high temperature zone of the apparatus.

Experiments in water/carbon dioxide mixtures were conducted in the subcritical, nearcritical and supercritical region of water. In contrast to the cellulose conversion experiments, a beneficial effect of the addition of carbon dioxide could not be detected. The results of these experiments are shown in Figure 12~~Figure 12~~~~Figure 12~~ together with the data for pure water as the reaction medium.

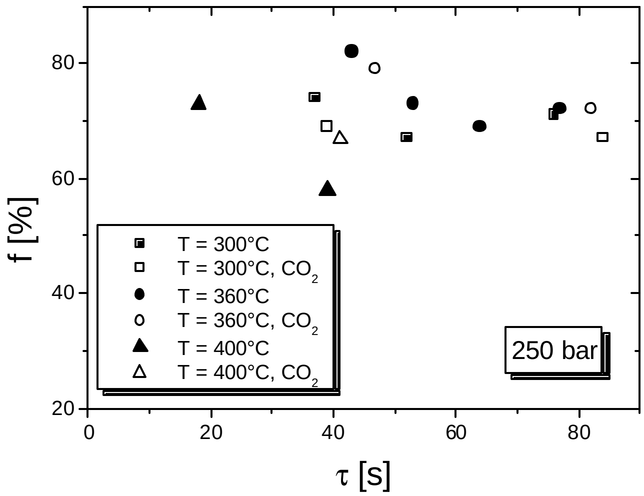

Figure 12~~12~~~~12~~: Wheat straw conversion in water, water/carbon dioxide

A difference in the degree of liquefaction on a carbon basis could not be determined within the range of experimental uncertainties, meaning that a residual portion of the wheat straw is not as susceptible to changes in pH as cellulose is at the conditions applied.

The results of the experiments with wheat straw did neither reveal a distinct temperature dependence nor a clear influence of reaction time. The results in terms of the degree of liquefaction are depicted in Figure 13~~Figure 13~~~~Figure 13~~.

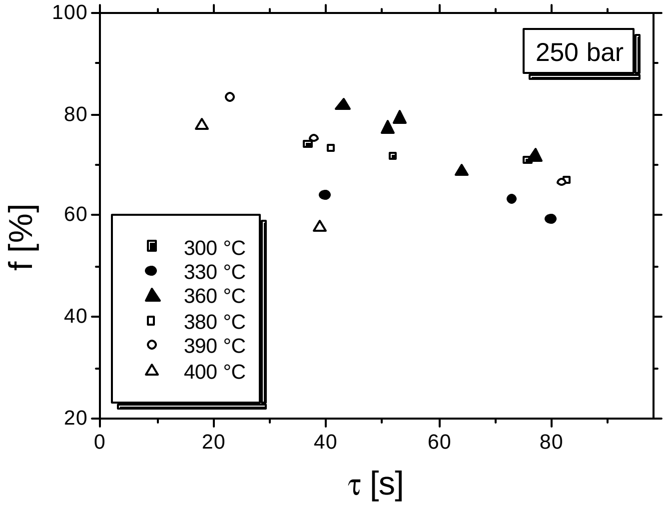

Figure 13~~13~~~~13~~: Conversion of wheat straw to water-soluble substances

In average a portion of about 20-30 % of the influent carbon could not be converted to water-soluble carbon, independently of temperature. This fraction is in the order of the lignin content of wheat straw, which amounts to roughly 20 % of the total carbon. Furthermore it appears that the degree of conversion in average slightly decreases with increasing reaction time. One possible explanation for this observation may be the evolution of carbon-bearing gas species. Another reason might be the renewed formation of carbon-rich, insoluble material due to the repolymerisation of reactive radicals at higher temperatures and residence times.

In addition to the fully-continuous experiments a number of runs were conducted in fixed bed mode. For these experiments it was initially intended to calculate the degree of conversion by determining the weight loss of the solids trapped in the fixed bed. The results however showed that this approach was not feasible due the fact that essentially all solid particulates dissolved in water at operating conditions. The effluents were therefore collected in different fractions and analysed for the concentration of dissolved organic carbon.
The results reveal that the main part of the carbon is collected in the first fraction during the heating up of the fixed bed to the desired holding temperature, while in the second, constant temperature phase only a very minor carbon concentration could be detected. Presumably, the carbon is successively converted to water-soluble substances during the heating up phase and instantaneously cooled down in the subsequent cooler. The effluent analysis of two runs with holding temperatures in the near-critical region is depicted in Table 2~~Table 2~~~~Table 2~~.

T [°C]	380	375
f [%]	~ 93	~ 100

Table 2~~2~~~~2~~: Degree of wheat straw conversion in fixed bed mode

In these experiments a degree of liquefaction of close to 100 % could be obtained. These results support the assumption that the degree of liquefaction decreases with progressive reaction time at higher temperatures.

A detailed characterization of the solubles released during the liquefaction by means of HPLC and GC analysis was not attempted for the wheat straw degradation but restricted to the model compound studies with pure cellulose and lignin.

Could you please provide us a list of the compounds produced during liquefaction of wheat straw ? As well as their relative abundance (if possible)?

3.3 Lignin Degradation

The second additional conversion technology to be tested in the second project phase is the oxidation of biomass in near/supercritical water. Lignin was chosen as a model compound for real biological waste, since lignin constitutes the most persistent component of plant derived biomass.

Water-insoluble organosolv lignin (purchased from Aldrich) was treated in fixed bed mode at nearcritical, non oxidative conditions to gain information about the achievable degree of liquefaction by hydrothermolysis. In the first experiments the effluents of the fixed bed were directly passed to the double-pipe heat exchangers and thus cooled down immediately. With this operating mode and preset holding temperatures of 370°C-380°C degrees of liquefaction in the range of 20-25 % could be achieved. A mass balance check yielded an essentially complete recovery of total carbon in the effluent, which in turn means that the lignin became water-soluble in nearcritical water and passed the sinter metal inlet (mean pore diameter ~0.5 µm). At ambient conditions, however, about 75 % of the carbon were present in form of a water-insoluble, very finely suspended phase.

Subsequently, the high temperature oven was connected to the outlet of the fixed bed in order to extend the working temperature and the residence time of the effluents in the operating zone. With this set-up outlet temperatures up to 500°C could be realized. The results of these experiments show that the temperature increase led to an increase in degree of liquefaction up to 40 % at an outlet temperature of 450°C, while at even higher temperatures the degree of liquefaction seems to be inversely affected by temperature, which is probably due to the formation of product gas.

Based on these results, the feasibility of producing solid-free effluents by adding a proper oxidant was to be proven. In these preliminary experiments, hydrogen peroxide was added at a stoichiometric excess of 1.5 to water-soluble alkali-lignin directly into the feed container, meaning that the oxidant was introduced together with the biomass. The results of these experiments in terms of the recovery of dissolved carbon in the effluent are summarized in Table 3~~Table 3Table 3~~.

T_{out} [°C]	365	390	419	489
f [%]	8.3	8.7	13.0	10.8

Table 3~~33~~: Recovery of dissolved carbon for alkali lignin oxidation experiments; P = 250 bar, t **~[s]**

The concentration of alkali lignin employed in these runs was 1-2 wt-% . The effluents of these experiments were colourless and absolutely solid free, while in case of the non oxidative treatment a dark colour and a water-insoluble phase could be observed. During the processing of the feed suspension a vigorous gas evolution could be detected, but was not determined quantitatively.

The residual fraction of dissolved organic carbon with respect to the total influent carbon (completely soluble) was in the range of 10 % for all experiments depicted in the table. However, it has to be taken into account that the residence time within the reactor decreased with increasing temperature. Given the reactor geometry, the residence time within the reactor was in the range of a few seconds.

Having shown the feasibility of drastically decreasing the dissolved carbon of water soluble lignin by adding an oxidant, a few tests of this technology using insoluble wheat straw have been conducted. Again, the effluents of the SCWO-treatment were absolutely solid free and colourless. For an outlet temperature of 370°C a degree of liquefaction of 24 % was determined, meaning that about 75 % of the initial carbon have been gasified in the course of the oxidation. For future experiments a quantitative gas analysis will be installed for checking the mass balances.

4 CONCLUSIONS / OUTLOOK

Based on the results of the second project phase so far, the oxidative treatment of persistent biomass constituents seems to be a promising supplementary means for converting the residues of the ESA-substrate. While the addition of carbon dioxide to lower the pH exhibits a catalyzing effect in the liquefaction of pure cellulose, it did not prove to be as efficient in the conversion of wheat straw. Although close to complete degrees of liquefaction could be achieved by hydrothermolysis, it was not possible to obtain absolutely solid free effluents. This aim could however be achieved by Supercritical Water Oxidation of water-soluble lignin and insoluble wheat straw. In case of lignin, the dissolved organic carbon could be reduced by 90 % without the formation of any insoluble matter. In case of wheat straw, the solid-free effluents had a dissolved organic carbon content of 25 % with respect to the influent suspension.

In the next step the study of the biomass conversion by SCWO will be systematically continued. The future tasks will include the quantitative measurement of the gas phase in terms of composition and quantity for closing the carbon balance. A GC-MS method for the determination of aromatic species in the liquid phase is, in principle, available but needs to be refined.
In accordance with the Work Packages, the non-degradable effluents from the methanogenic unit of Partner 1 will be subjected to oxidation in supercritical water.
In the medium-term it is planned to modify the oxidant supply by activating a high pressure/ high temperature electrolysis cell for the in-line production of oxygen.