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Technical Note 86.4.4
on the MAP-Project
"A Total Converting and Biosafe Liquefaction Compartment for MELISSA"

Work Package 4.400: Subcritical Degradation

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1 Introduction

This technical note presents the current state of the MAP project "A Total Converting and Biosafe Liquefaction Compartment for MELISSA" on behalf of the Department of Thermal Process Engineering, Technical University of Hamburg-Harburg. Beginning with a brief outline of the objectives of the final stage of the project, this paper covers the presentation of modifications to the experimental apparatus for a continuous supply of carbon dioxide to the influent suspension. This part is followed by a section presenting the latest results of the hydrothermal treatment of cellulose in the systems H_2O and H_2O/CO_2 at subcritical conditions. In this context, the degrees of liquefaction and the respective yields of main degradation products are given. An approach modelling the cellulose conversion applying a first order kinetic is given. The technical note concludes with a summary of the tasks completed in accordance with the work package description (WP. Ref. 4.400) and the additional tasks agreed on at the 3rd Progress Meeting in Hamburg.

2 Objectives

In the first three stages of the project the applicability of the hydrothermal degradation of biomass at elevated temperatures and pressures could be proven. Pure cellulose could completely be converted to water-soluble substances within residence times of less than 30 seconds at temperatures exceeding 300°C. Regarding the real biomass samples obtained from the methanogenic reaction unit of Partner 1, the experiments revealed the presence of a residual solid fraction which could not be completely liquefied at the operating conditions applied so far. Therefore, it was agreed on at the 3rd Progress Meeting in Hamburg that the solid biomass, which could not further biologically be degraded in the mesophilic methane reactor, was first to be treated in the fibrobacter compartment of Partner 2 before being processed to the high temperature tubular reactor at the Department of Thermal Process Engineering at the Technical University of Hamburg-Harburg. The results of these 3rd loop experiments in terms of degree of liquefaction are not included in this technical note but will be available before the end of the final phase of the project.

In addition, the application of supplementary means to promote the degradation of fibrous biomass in nearcritical water is envisaged. These complementary methods, which were not originally subject of the first project phase, include the advanced hydrolysis of biopolymers by acidification with carbon dioxide and the partial oxidation of the recalcitrant biomass fraction by means of a built-in electrolysis cell. Experiments utilising carbon dioxide to lower the pH-value of the influent suspension and catalyse the hydrolytic cleavage of the biopolymers were conducted during the last stage of the first phase of the project, while the oxidative treatment is intended for the prolongation phase. The results of these experiments along with the experiments using pure water are depicted in this technical note.

3 Materials and Methods

3.1 Modifications of the experimental apparatus

The modified experimental set-up is illustrated in Figure 1.

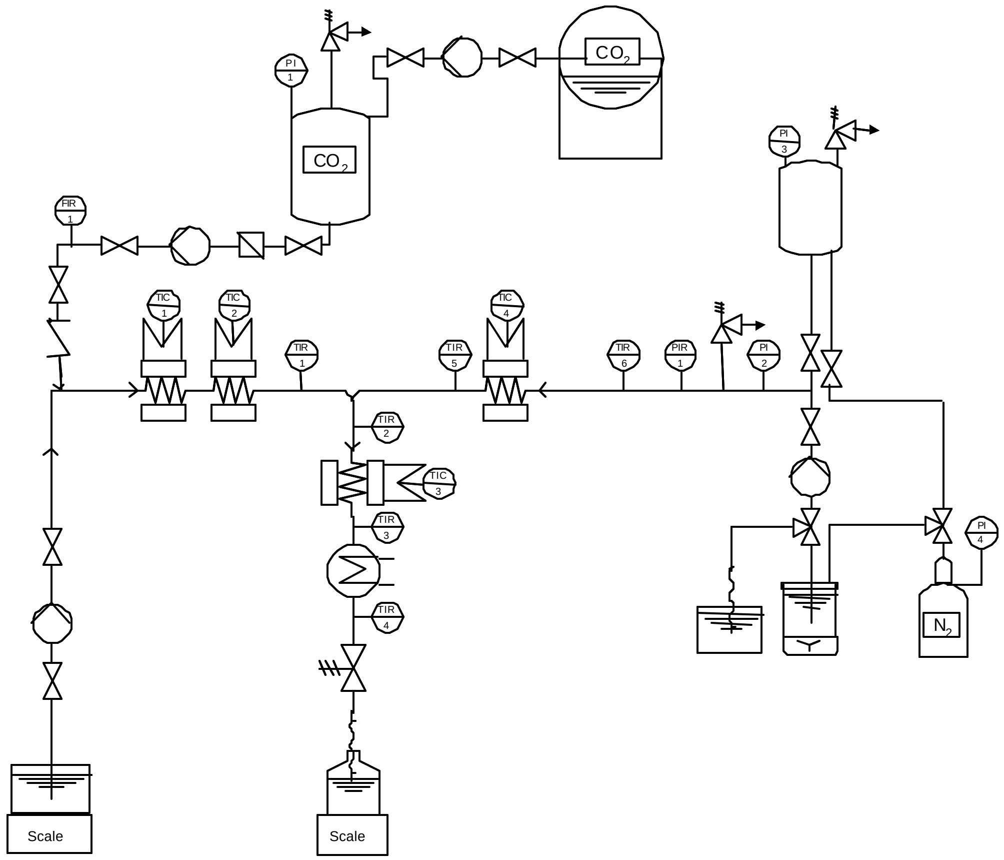

Figure 1: Modified experimental set-up of the tubular reaction unit

In addition to the modifications described in the previous technical note, namely the introduction of a mixing point to minimise the temperature difference between the reactor inlet and outlet and to ensure isothermal reaction conditions, a carbon dioxide supply was established. Gaseous carbon dioxide is delivered from a CO_2-storage tank. It passes a cooler where it is liquefied and it is subsequently processed to a 1 litre autoclave by means of an airdriven pump. The CO_2 mass flow is adjusted by a HPLC pump, which is guarded from impurities by an inline filter. Prior to a second mixing point, where the carbon dioxide is introduced to the pure water flow, the CO_2 is passed through a mass flow meter to accurately determine the amount of CO_2 added to the system.

3.2 Substrates/Analytical procedures

The materials employed in the experiments as well as the procedures to determine the degree of liquefaction and the respective amounts of main degradation products have been described in detail in the preceding technical notes. The experimental approach remained unchanged except for the analytical method for the determination of carboxylic acids. These analyses were conducted at Partner 3 with a gas chromatograph (Varian GC 3900), equipped with a fused silica column (Chrompack WCOT 25MXO) and a flame ionisation detector.

The samples were acidified by H_3PO_4 to pH 2 before injection into the gas chromatograph. This method is capable of analysing carboxylic acids higher than formic acid, including acetic acid, propionic acid, and n-butyric and isobutyric acid.

4 Results and discussion

4.1 Liquefaction of pure cellulose

Cellulose degradation experiments were performed over a wide range of operating conditions, covering temperatures from 250°C to 380°C and pressures from 150 bar to 250 bar, at initial solid concentration of 0.5 and 0.75 wt-%. In addition, different concentrations of carbon dioxide with respect to the degree of saturation at given experimental conditions were employed in order to elucidate the potential of carbon dioxide to catalyse the cleavage of the glycosidic bonds by lowering the pH of the system. These experiments were conducted in the modified experimental set-up, which allows more meaningful conclusions with regard to the reaction kinetics due to the well-defined operating conditions.

4.1.1 Influence of operating pressure

The operating pressure induces a possible influence on the cellulose degradation by affecting the fluid density, thus influencing physical-chemical properties like the dielectric constant and the ionic product. In order to study the effect of pressure changes at constant temperature, experiments were conducted at 250°C and 290°C and pressures of 150 bar, 200 bar, and 250 bar, respectively. The influence of the pressure on the rate of liquefaction is depicted in Figure 2.

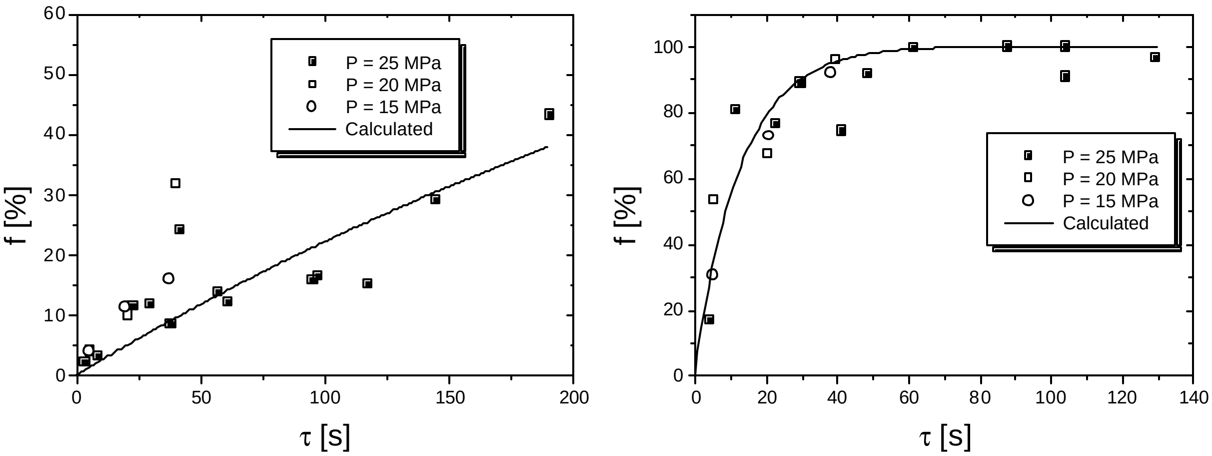

Figure 2: Influence of pressure on the degree of liquefaction: T = 250°C (left), T = 290°C (right)

The curves illustrated in the above figures were obtained by modelling the cellulose conversion at a pressure of 250 bar by a first order kinetic. This approach is explained in more detail in the section covering the temperature dependence of the degradation.

It can be inferred that the experimental pressure exhibits a very minor, negligible influence on the rate of conversion based on the liquefied carbon. This may possibly be explained by the fact that the pressure dependency of water density is relatively weak in the temperature range employed in these experiments. The data points at a temperature of 250°C and residence times of about 40 seconds appear to be experimental errors.

4.1.2 Influence of operating temperature

The experimental temperature was varied over a broad range in order to study the temperature dependence of the rate of liquefaction up to nearcritical conditions. Since it was known from previous experiments that the cellulose decomposition can be considered as being completed within seconds at temperatures markedly exceeding 300°C, the focus of this parameter study was laid on the temperature region from 250°C to 310°C.

The degree of liquefaction in the course of reaction at 250°C and 270°C is shown in Figure 3.

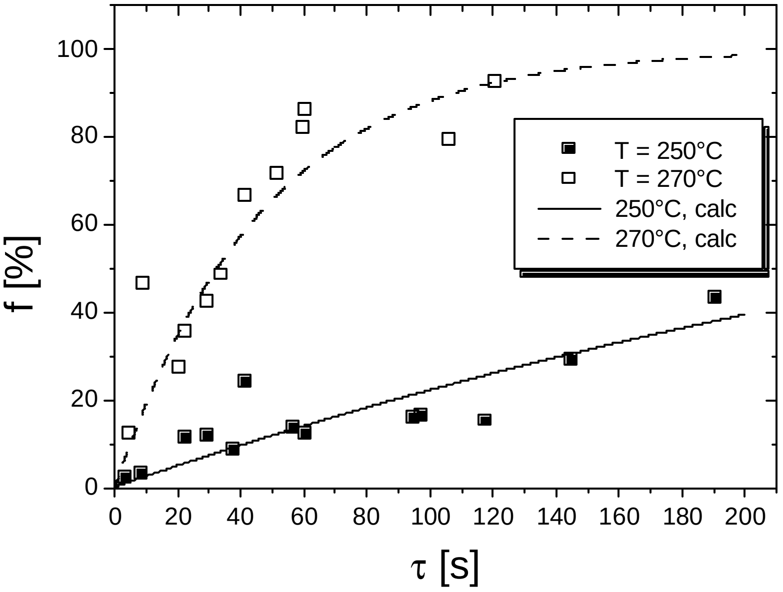

Figure 3: Degree of liquefaction versus time, P = 25 MPa

It can be concluded that at an experimental temperature of 250°C degrees of conversion of 30-40 % could be achieved within residence times of 3 minutes. An increase in temperature to 270°C results in a much more rapid reaction, leading to a close to complete conversion at residence times of about 2 minutes. Increasing the operating temperature further, results in an even faster cellulose degradation based on the dissolved carbon. This behaviour is depicted in Figure 4 for temperatures of 290°C and 310°C, respectively. At 290°C, the cellulose is completely converted into water-soluble substances within 1 minute, while at a temperature of 310°C the liquefaction takes less than half a minute according to the data points.

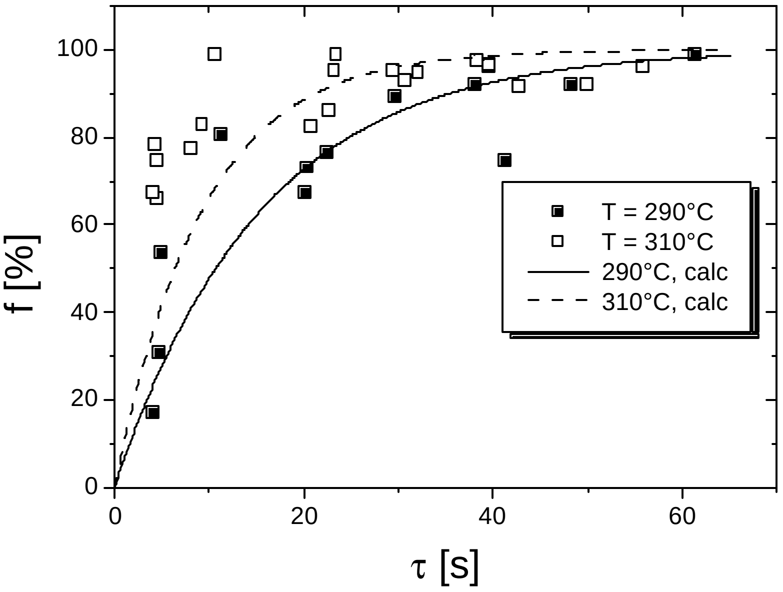

Figure 4: Degree of liquefaction versus time, P = 25 MPa

At 310°C, the calculated curve exhibits slight variations from the course depicted by the data points. Here it seems that the reaction proceeds even faster than indicated by the calculated curve.

The kinetic of the cellulose degradation was modelled by a first order approach. For such an irreversible reaction the conversion can be described by the following equation:

$$f = 1 - \exp(-k \cdot t)$$

where f is the degree of liquefaction and k denotes the reaction rate constant. This expression can be rearranged as follows:

$$\ln(1 - f) = -k \cdot t$$

such that a linear relationship is obtained if the reaction is first order. The experimental results are illustrated as the natural logarithm of (1-f) versus τ in Figure 5.

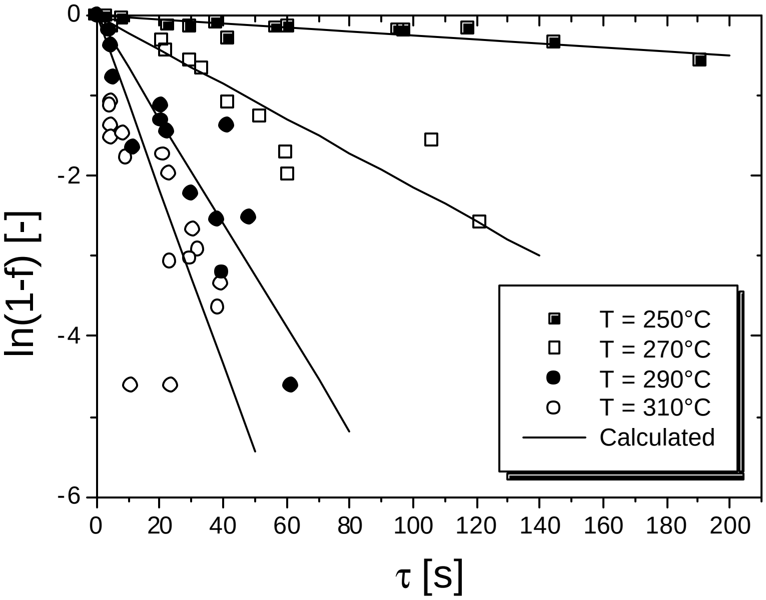

Figure 5: Evaluation of cellulose degradation rate constants

The results show a linear relationship such that the reaction kinetic can be described by a first order approach. The respective value of the reaction rate constant can be derived as the slope of the straight lines by linear regression. The values are summarised in Table 1.

T [°C]	250	270	290	310
k [1/s]	0.0025	0.0214	0.0647	0.1086

Table 1: Reaction rate constants as obtained from linear regression

A well known approach to describe the temperature dependence of the rate constant is the expression developed by Arrhenius:

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

with k_0 being the pre-exponential factor and E denoting the activation energy. Plotting ln(k(T)) versus the reciprocal of temperature should therefore yield a linear relationship. Figure 6 depicts the results of applying Arrhenius' law to the experimentally derived rate constants.

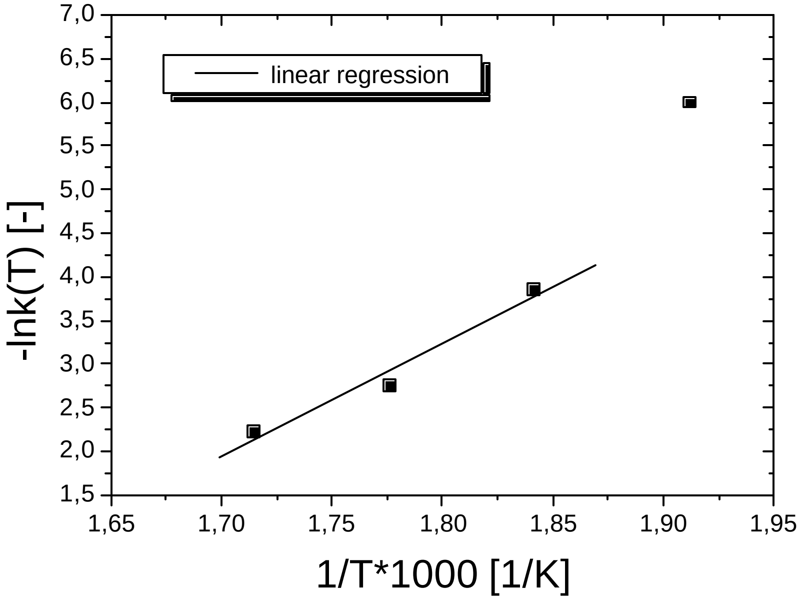

Figure 6: Temperature dependence of the reaction rate constant

The temperature dependence of the cellulose degradation constant cannot reasonably be described over the whole temperature range from 250°C to 310°C but seems to exhibit a sharp bend in the region around 270°C. Such a behaviour could be explained by kind of a limitation, which leads to an increased apparent activation energy, and which is overcome at higher temperatures. For temperatures ranging from 270°C to 310°C the data points can be represented by a linear relationship as suggested by Arrhenius' law.

4.2 Product formation

The liquid effluents of the hydrothermal treatment were analysed for saccharides and secondary degradation products thereof as well as for carboxylic acids. Main degradation products encountered in the effluents were glucose, pyruvaldehyde, hydroxymethylfurfural and acetic acid. The respective yields of these main degradation products are illustrated in Figure 7 on a carbon basis.

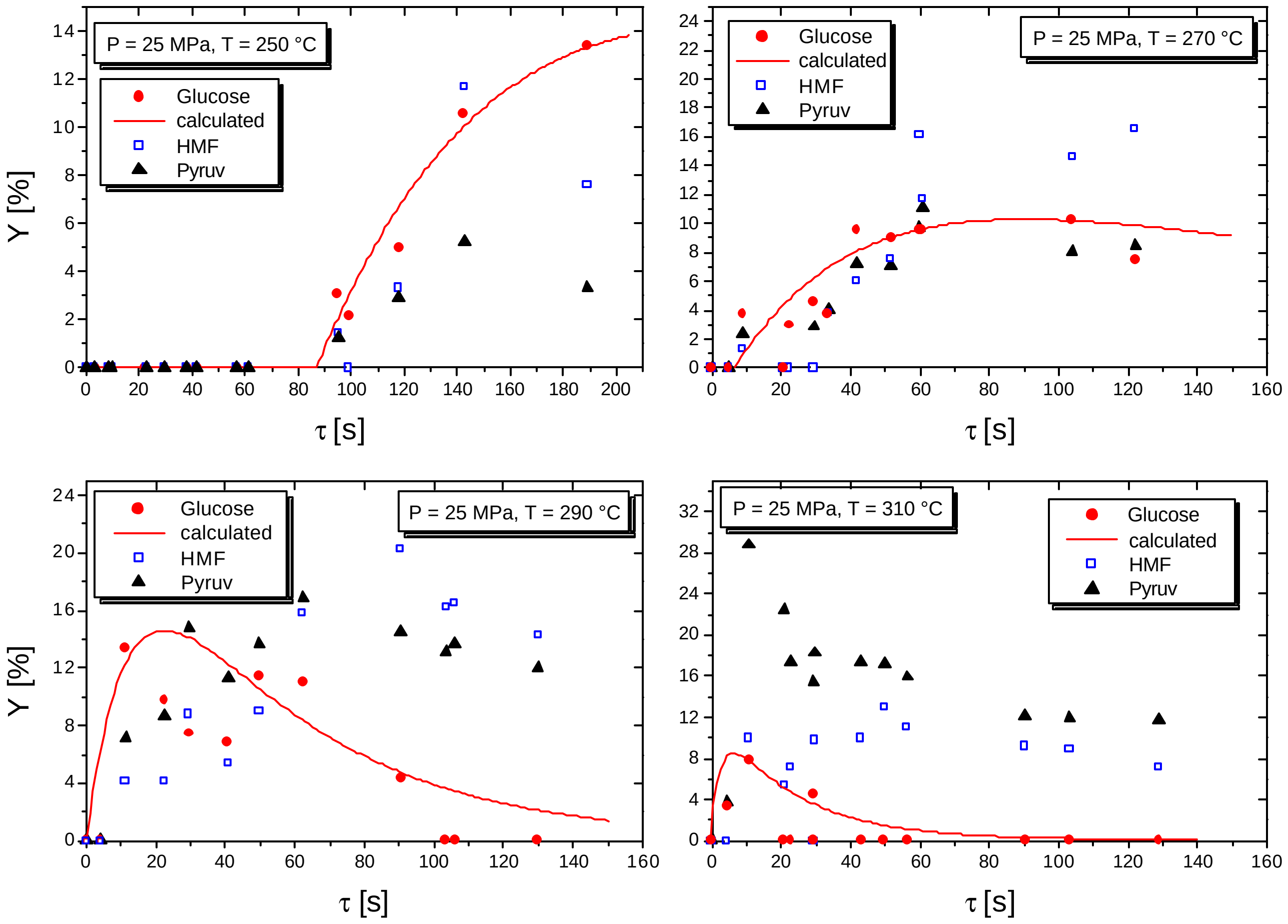

Figure 7: Yields of main degradation products: glucose, hydroxymethylfurfural (HMF), pyruvaldehyde, P = 250 bar

The curves describing the glucose yields were obtained by assuming that glucose is subjected to consecutive reactions, with formation and secondary reactions being of first order kinetic. This approach is illustrated in the scheme below:

$$\text{Cellulose} \xrightarrow{k_{G,f}} \text{Glucose} \xrightarrow{k_{G,d}} \text{Secondary products}$$

With subscript f denoting formation and d denoting decomposition.

Cellulose decomposition rate constants were taken from [1].

As for the glucose yields, a maximum can be observed due to consecutive degradation reactions. This maximum is shifted to shorter residence times with increasing temperature. At higher temperatures, pyruvaldehyde and HMF become the most important products, though it may be concluded from the data that these substances are subject to further degradation at higher temperatures and residence times, as indicated by the slight decline of the respective product yields.

Samples of selected experimental runs were analysed for carboxylic acids. Acetic, propionic and isobutyric and n-butyric acid were detected in these samples. However, only acetic acid had a significant contribution to the total carbon of the effluents.

The ratio of carbon bound in acetic acid to the total effluent carbon is depicted in Figure 8 versus time.

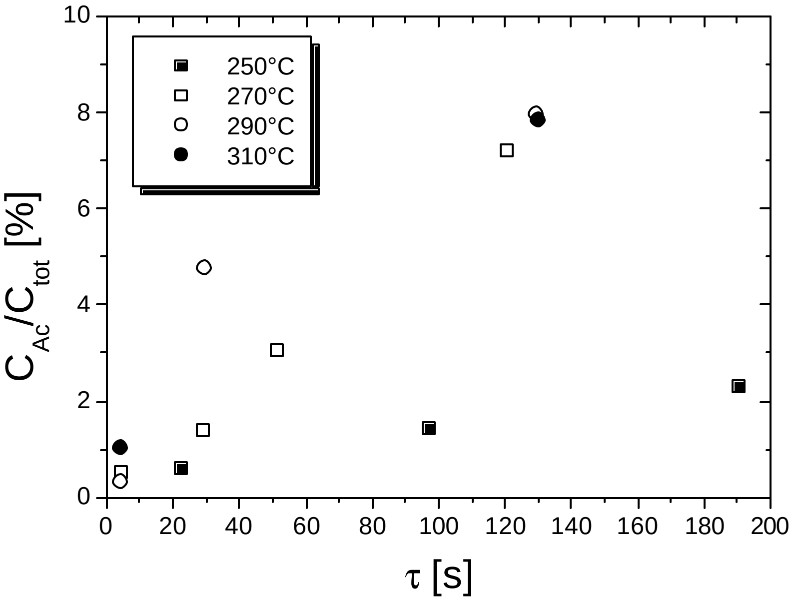

Figure 8: Acetic acid concentration in terms of carbon, P = 250 bar

The results reveal the presence of considerable amounts of acetic acid, which may be an explanation for the marked decrease in pH of the effluents. This is especially valid for temperatures higher than 250°C, where the course of acetic acid content shows a steep increase with residence time. The amount of acetic acid over time shows an approximately linear relationship. However, more samples need to be analysed for acetic acid to provide a more detailed study of the kinetic.

4.3 Acidification by carbon dioxide

As described previously the addition of carbon dioxide to water at elevated temperatures and pressures leads to a significant decrease in pH due to the increased solubility of carbon dioxide. This property could be exploited to promote acid-catalysed degradation steps such as the hydrolytic cleavage of glycosidic bonds without adding mineral acids. Using carbon dioxide bears the advantage of easily regenerating the CO_2 by expansion, such that neutralisation and precipitation steps become obsolete. Cellulose degradation experiments using different amounts of carbon dioxide with respect to the level of saturation were conducted to study this appealing concept. Equilibrium data for the system H_2O/CO_2 were taken from [2] and [3]. While at temperatures exceeding 250°C the effect of carbon dioxide addition was diminishing, a marked influence on the rate of liquefaction and product formation could be observed at 250°C.

The degree of conversion to water-soluble substances at different carbon dioxide contents with respect to saturation is shown in Figure 9.

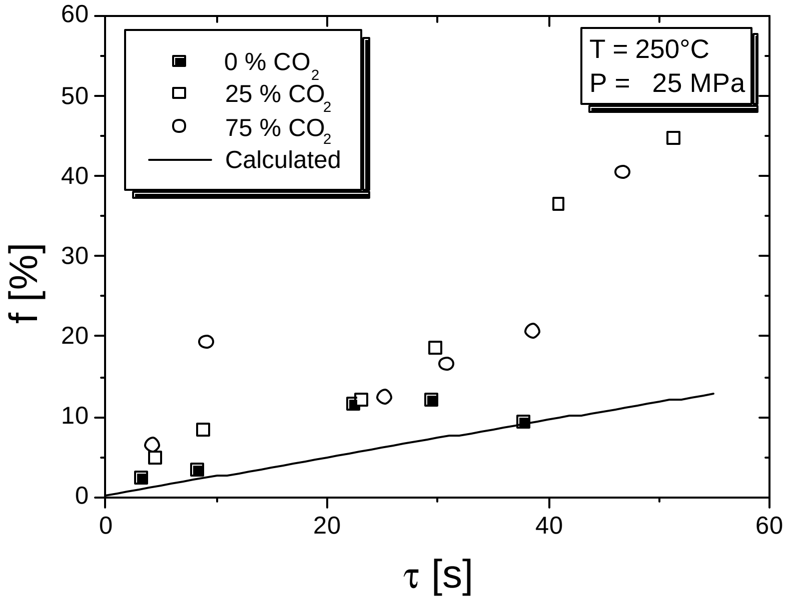

Figure 9: Degree of liquefaction at different degrees of saturation

The addition of carbon dioxide leads to significant increase in cellulose conversion. While the degree of liquefaction is about 10 to 15 % at a reaction time of 50 seconds in pure water, the conversion goes up to 40 to 50 % in the system H_2O/CO_2 at comparable residence times. The degree of saturation seems to have a minor influence on the rate of conversion, which may be explained by the fact that the difference in pH increasing the level of saturation from 25 to 75 % is comparatively small.

The effect of carbon dioxide addition can also be observed with regard to the product formation. This influence is especially noticeable with respect to the course of glucose formation. Figure 10 shows the ratio of carbon bound in glucose to the total amount of carbon introduced in the reactor.

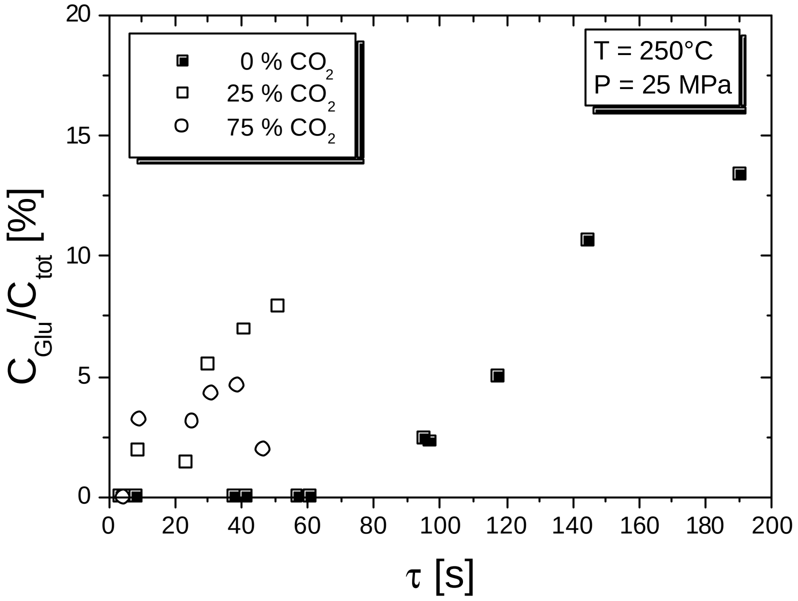

Figure 10: Relative glucose concentration at different carbon dioxide contents

The addition of carbon dioxide results in glucose formation at much shorter residence times compared to pure water. Again, no difference between degrees of saturation of 25 % and 75 % can be detected within the experimental accuracy.

5 Summary

A detailed parameter study on the liquefaction of pure cellulose in sub- and nearcritical water has been conducted with the modified experimental set-up during the last phase of the project. While the operating pressure exhibits a negligible influence on the rate of conversion, the operating temperature strongly affects the reaction kinetic. It could be shown that cellulose can be readily converted into water-soluble substances within seconds at temperatures exceeding 300°C. Furthermore, the cellulose decomposition in water at elevated temperatures and pressures could be proven to follow a first order kinetic. The temperature dependence of the reaction rate constant can be reasonably described by an Arrhenius relationship in the temperature range from 270°C to 310°C, while the rate constant is markedly lower at 250°C. Such a behaviour may be explained by some type of transport limitation. However, further experiments in the relevant temperature range are necessary to fully describe this phenomenon.

In addition to the degree of conversion, the determination of main degradation products was continued. As a result, saccharides and secondary decomposition products thereof as well as carboxylic acids have a major contribution to the dissolved organic carbon. Experiments using carbon dioxide to decrease the pH value of the influent suspension and promote the acid catalysed cleavage of the glycosidic bonds reveal an increased rate of conversion at 250°C.

Future perspectives:

As discussed at the 3rd Progress Meeting in Hamburg, July 4th 2002, the hydrothermal treatment of solid residues from the fibrobacter compartment of Partner 2 is to be done. These experiments are currently conducted at the Department of Thermal Process Engineering and are therefore not included in this paper. The results of these runs in terms of liquefied carbon will be available before the end of the project and will be send along with the effluents to Partner 1.

Literature:

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1 Liu, K.: Zur Hydrolyse von Biopolymeren in Wasser und Kohlendioxid unter erhöhten Drücken und Temperaturen, Technische Universität Hamburg-Harburg, Dissertation (2000)

2 Takenouchi, S.; Kennedy, G.C.: The binary system H_2O/CO_2 at high temperatures and pressures, Am. J. Sci. (1964), pp. 1055-1073

3 Gmelin, L; Fluck, E.: Gmelin handbook of inorganic chemistry (1975) Vol. 14: Carbon, Springer, Berlin