

PRODUCTION OF VALUABLE ORGANIC COMPOUNDS BY HYDROLYZING BIOPOLYMERS IN WATER AT ELEVATED TEMPERATURES AND PRESSURES

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The hydrothermal treatment of biomass in a tubular reactor operated at elevated temperatures and pressures has been investigated. Both model compounds like cellulose and real biomass obtained from a mesophilic biogas reactor have been studied with respect to the degree of conversion to water-soluble substances and the main degradation products. A parameter study covering a wide range of conditions was employed to show the feasibility of the hydrothermal degradation to rapidly liquefy these recalcitrant, poorly biodegradable materials at high space-time-yields. The experimental temperature was varied from 250°C up to 400°C at operating pressures ranging from 150 bar to 250 bar and residence times from a few seconds up to 3 minutes.

Based on the experimental data, a global approach assuming a first order kinetic model was used to describe the rate of cellulose conversion to water-soluble matter. In addition to the studies with pure water, experiments using water/carbon dioxide mixtures were conducted to investigate the influence of the decrease in pH caused by the carbon dioxide on the reaction rate and product formation.

INTRODUCTION

Water at elevated temperatures and pressures has been gaining increasing attention as both a solvent and reaction medium for organic material in the past decade. Based on its specific physico-chemical properties, which can be altered and adjusted over a wide range of conditions, supercritical water has been established as a medium for the oxidation of organic wastes. While this process is aimed at complete oxidation of the influents and is mainly applied to hazardous substances, recent studies are elucidating the appealing concept of near-critical water as a medium for the selective production of chemical species, which cannot - or only at rather low space-time yields - be synthesized by alternative chemical processes. As such, the partial oxidation and the hydrolysis of organic substances appear to be the most promising approaches.

Water at near-critical conditions exhibits some unique features which make it a promising solvent and reaction medium for a wide variety of applications. This distinctly different behavior compared to water under ambient conditions is due to the dramatic changes in physical properties. The significant drop in the dielectric strength [1] contributes to a much increased solvent power for most organic compounds, thus providing a homogeneous reaction

atmosphere. In such cases no phase boundaries impose any mass transfer limitations on the reactions and more chemical bonds are accessible to reaction steps.

Due to its elevated temperatures, near-critical water provides a thermally activated regime for fast kinetics. Depending on the system pressure and temperature the ion product of water K_w drastically increases from a value of 10^{-14} at ambient conditions to 10^{-11} at subcritical temperatures [2], while at supercritical conditions the ion product decreases to values down to 10^{-23} . As a result of this drastic change in the near-critical region, many ionic reaction pathways, e.g. acid and base catalyzed hydrolysis reactions, exhibit a maximum at subcritical temperatures.

Water at elevated temperatures and pressures offers the attractive opportunity to convert biomass to water-soluble species at high rates of reaction without the use of any additional chemicals, namely mineral acids or bases as catalysts. The hydrolysis of biopolymers, being the first step to obtain useful products, often proves to be the rate limiting step in biological treatment methods. Therefore, the treatment of biomass in sub- and nearcritical water could either be employed to directly produce valuable products or it could be established as a pre-treatment to supply an appropriate feedstock for subsequent biological utilization.

Within the scope of this work, the feasibility of producing valuable organic compounds by hydrolyzing biopolymers in sub- and nearcritical water is being studied. Different biopolymers like cellulose, for the production of mono-saccharides and useful degradation products thereof, and polypeptides, for the depolymerization into amino acids, are being studied. The overall degree of conversion of the biopolymer as well as the yield and selectivity of the main reaction products are determined experimentally in a flow through type reactor. Additional means like the acidification by carbon dioxide [3] to lower the pH and promote acid catalyzed hydrolysis steps are being investigated. These studies are intended to investigate the feasibility of hydrolytic conversion of biological wastes into valuable end products in sub- and nearcritical water as a sustainable alternative to conventional degradation processes for biopolymers.

MATERIALS AND METHODS

Materials: Micro-crystalline cellulose was purchased from Merck (Avicel®) and was used as received. Real biomass samples were obtained from a mesophilic biogas reactor run at a hydraulic residence time of 20 days, the biomass being the non-biodegradable residues of the process. The solid residues were ground in a rotary cutter to a particle size of less than 250µm prior to the experiments. Demineralized tap water was provided by the water supply system of the Technical University Hamburg-Harburg.

Analytical procedures: The elementary composition of solid material was analyzed with a C/N/S-analyzer (Leco-2000-CNS). Regarding the biomass, a successive hydrolysis of the material following a standard procedure was conducted to specify the composition with respect to total fibres, cellulose, and lignin. Liquid effluents were filtrated using 0.45 µm filter units and analyzed for the dissolved organic carbon (DOC) using a TOC-analyzer (Elementar-highTOC +TNb).

Identification and quantification of saccharides and degradation products thereof was accomplished by HPLC analysis (LEC-column with RI-detection). In addition, liquid samples were analyzed for carboxylic acids.

Tubular reaction unit: The experimental set-up is schematically illustrated in Figure 1. The main building blocks of the apparatus are the feed supply vessel, the feed pump, the tubular reactor, and the downstream processing units, which consist of a double-pipe heat exchanger, an expansion valve, and the effluent collection system. The high pressure reaction unit is designed as a tubular reactor made of high temperature resistant steel (o.d. = 6.35 mm, i.d. = 3.05 mm).

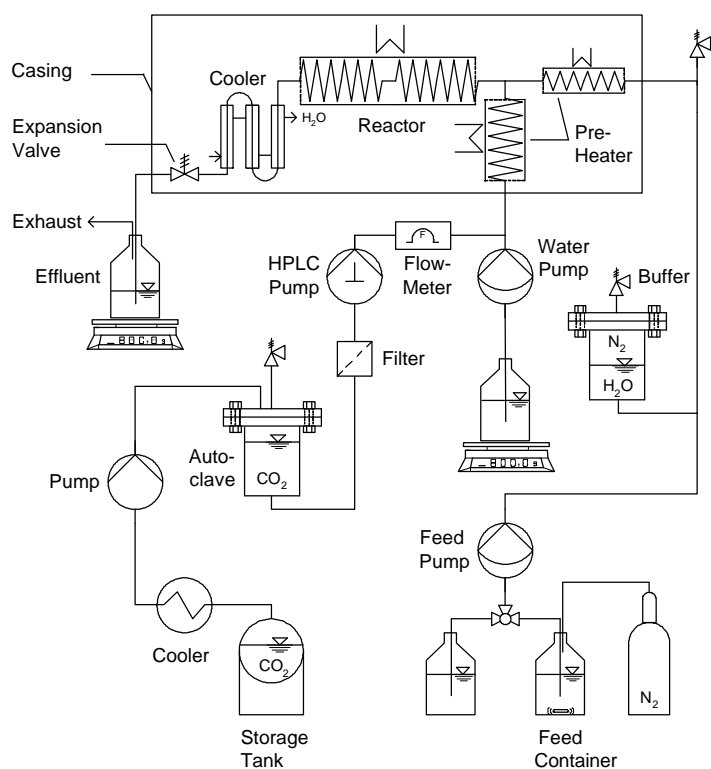


Figure 1 : Sketch of the experimental apparatus

Before entering the reaction unit the feed suspension is moderately preheated in an upstream coil. In order to ensure well-defined reaction conditions in terms of temperature and residence time, the reaction is started by mixing the feed suspension with a pure water stream, which is delivered into the system by a high pressure membrane pump and heated to high temperatures in a second pre-heater. The two pre-heaters and the reaction pipe are electrically heated by means of three heating jackets, which can be adjusted separately by a temperature control

system. In order to decrease the heat losses to the surroundings the complete high temperature section of the apparatus is thermally insulated.

The feed, which is agitated by a magnetic stirrer to ensure a homogeneous suspension, is put under a nitrogen headspace to avoid oxygen from entering the supply vessel. In order to minimize pressure fluctuations which are due to the operation of the membrane pumps and the expansion valve, a buffer vessel with a nitrogen headspace is connected to the apparatus. The mass flows are determined gravimetrically with laboratory scales.

Carbon dioxide is delivered from a storage tank, liquefied in a cooler and processed to an autoclave by means of an air-driven pump. Passing a filter unit, the carbon dioxide is introduced into the system by means of a HPLC pump. The amount of carbon dioxide is measured by a mass flow meter.

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RESULTS AND DISCUSSION

Cellulose degradation experiments using pure micro-crystalline cellulose were conducted to gain information about the rate of liquefaction and the yield of main degradation products for this most abundant plant constituent. While the operating pressure exhibits a negligible influence on the degree of liquefaction, the temperature markedly affects the rate of reaction.

This behaviour is illustrated in Figure 2, which depicts the degree of liquefaction on a carbon balance versus residence time at constant pressure.

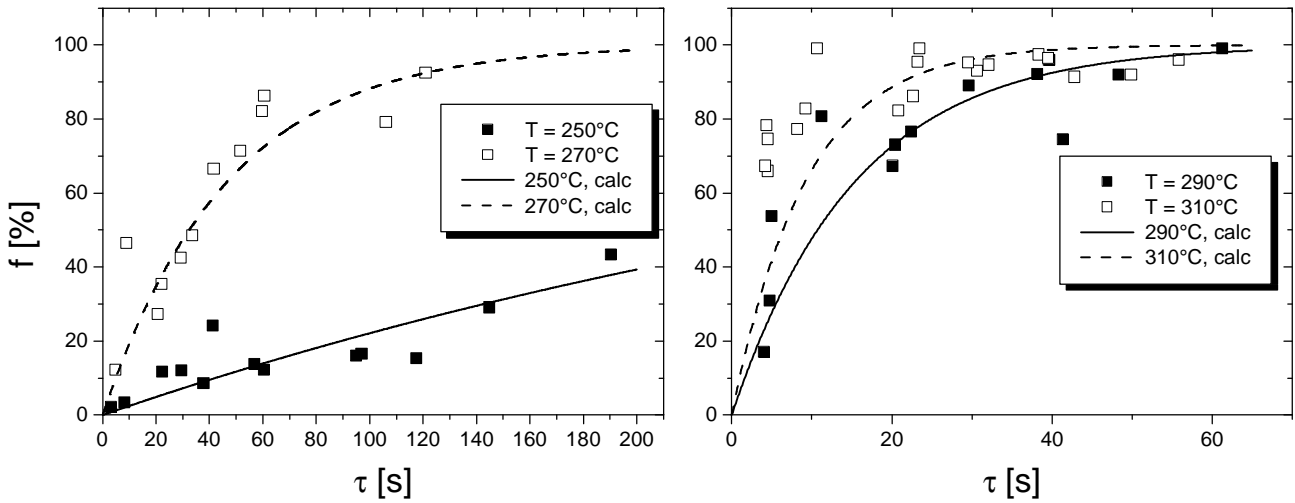


Figure 2: Degree of liquefaction f versus residence time τ at $P = 250$ bar

In this context, the degree of liquefaction was calculated as the ratio of dissolved carbon in the effluent to the total carbon of the influent suspension. The results reveal a strong increase of the rate of liquefaction with increasing temperature in the range of 250°C to 310°C, leading to a complete conversion to soluble products in less than half a minute at 310°C. A further increase in temperature results in an even more rapid degradation, yielding a complete conversion within seconds.

The calculated curves shown in the figure were derived assuming a first order kinetic for the cellulose decomposition. For this approach, the degree of conversion can be described by equation 1:

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

where k denotes the reaction rate constant of the cellulose hydrolysis. For a first order chemical reaction, plotting the left hand side of equation 1 versus the residence time yields a straight line with the reaction rate constant k being the slope, such that the rate constant of the cellulose decomposition can be derived by linear regression in case the reaction can reasonably be described by a first order approach.

A well-known approach to model the temperature dependence of the reaction rate constant is the equation developed by Arrhenius (equation 2)

$$k_{C,A}(T) = k_{0,C,A} \cdot \exp\left(-\frac{E_{C,A}}{R \cdot T}\right) \quad (2)$$

with $k_{0,C,A}(T)$ being the pre-exponential factor and $E_{C,A}$ denoting the activation energy of the reaction. In this case, the graph showing the rate constant on a logarithmic scale versus the reciprocal temperature is a straight line.

Figure 3 shows the curves obtained by applying the above concepts to the experimental data.

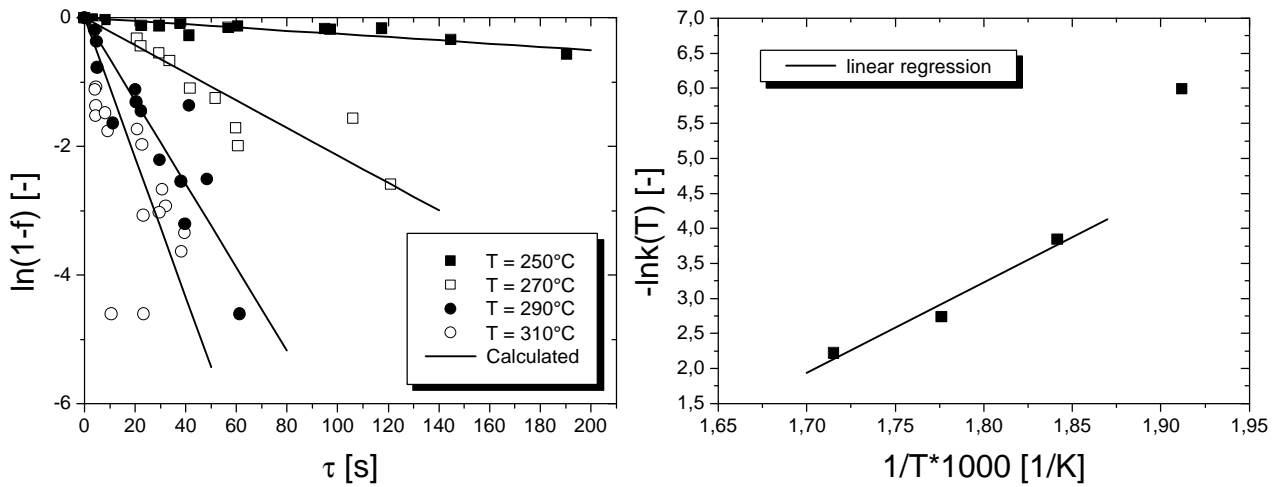


Figure 3: Determination of rate constants (left), Arrhenius plot (right), $P = 250$ bar

It can be inferred that the straight lines derived by linear regression reflect the respective data points reasonably well, thus justifying the application of a first order approach. Regarding the temperature dependence of the reaction rate constant, the rate constant at 250°C reveals a significant deviation from the linear relationship derived from the other data points. This behaviour might be contributed to some limitation, which is probably due to the crystalline structure and which results in a decreased apparent reaction rate constant.

The addition of carbon dioxide and the resulting decrease in pH leads to an increased rate of liquefaction and an earlier increase in glucose yield at 250°C compared to pure water as the reaction medium. The degree of liquefaction and the glucose yields during the course of the reaction are depicted in Figure 4.

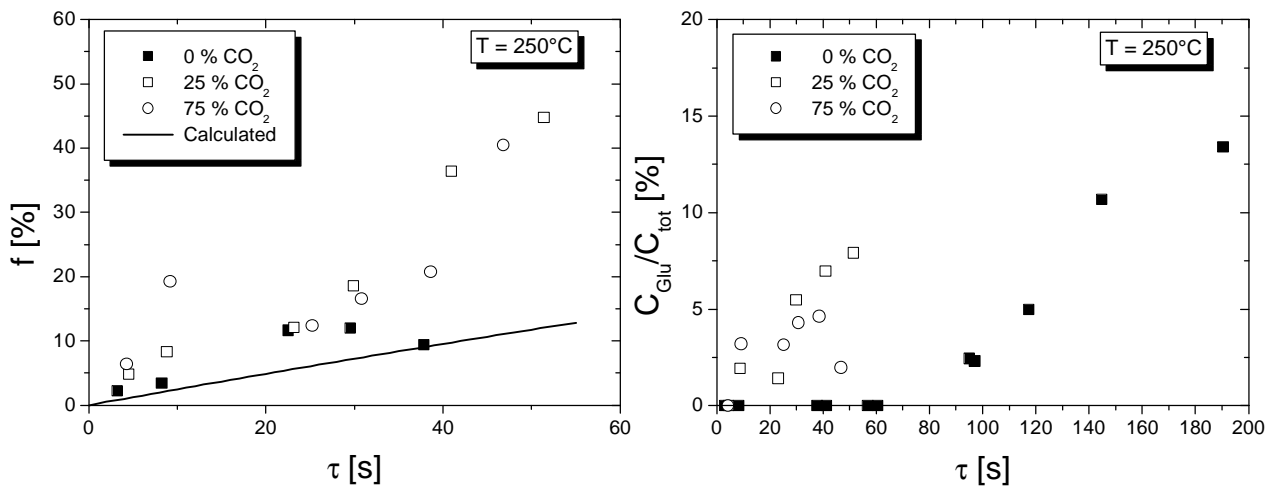


Figure 4: Degree of liquefaction (left), glucose yield (right), $P = 250$ bar

The amounts of carbon dioxide stated in the figure captions refer to the degree of saturation at given operating conditions.

In contrast to the hydrolysis of pure cellulose, the hydrothermal degradation of the biomass residues from the methane reactor yields an incomplete liquefaction, which can probably be attributed to the lignin present in the samples. As in the case of cellulose, the addition of carbon dioxide leads to a markedly increased rate of reaction. A more detailed investigation is subject of ongoing research work [4].

CONCLUSIONS

A detailed parameter study on cellulose conversion in sub- and nearcritical water has been conducted in order to investigate the reaction behaviour with respect to the rate of reaction and product formation. The cellulose degradation can be reasonably described by a first order approach. Regarding the product formation, mono- and oligosaccharides and decomposition products thereof as well as carboxylic acids could be identified. The respective yields depend on the operating temperature and the residence time.

The addition of carbon dioxide leads to a significant increase of the reaction rate at 250°C due to the decrease in pH of the system water/carbon dioxide. Additionally, this approach offers the advantage to easily recover the carbon dioxide by expansion and circulate it in order to catalyze the reaction.

Additional experiments employing proteins as a model compound and real biomass having a complex composition have been conducted to study the feasibility of the hydrothermal treatment both as a means to readily liquefy biopolymers and to generate useful products, either for direct applications or the utilization by micro-organisms in subsequent biological processes.

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