A TOTAL CONVERTING AND BIOSAFE LIQUEFACTION COMPARTMENT FOR MELLISSA

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Subcritical Degradation

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1 Outline

In this 1st technical note the progress of the project "A Total Converting and Biosafe Liquefaction Compartment for MELISSA" on the part of the Department for Thermal Separation Processes, Technical University Hamburg-Harburg, is reported. In a brief introductory section some fundamental aspects of supercritical fluid technology, including the definition of the critical state and the unique features of water at near-critical conditions are given. In the following sections the current state of the project is presented. Starting with a description of the high pressure tubular reactor the experimental and analytical procedures are explained. Subsequently preliminary results of the first experimental runs are discussed. The report ends with a summary of the tasks completed in accordance with the working plan (W.P.REF. 4.100) and a brief outlook of the activities to be performed in the next stage of the project.

2 Theoretical Background

2.1 Definition of the supercritical state

The supercritical state is defined as the state of a fluid above its critical temperature T_c and critical pressure p_c [1]. The critical point marks the end point of the vapor pressure curve, such that there is no two-phase region but a one-phase supercritical region at conditions above the respective critical values. The supercritical region is denoted as the hatched area in Figure 1, which depicts a schematic p-T-diagram of a pure component.

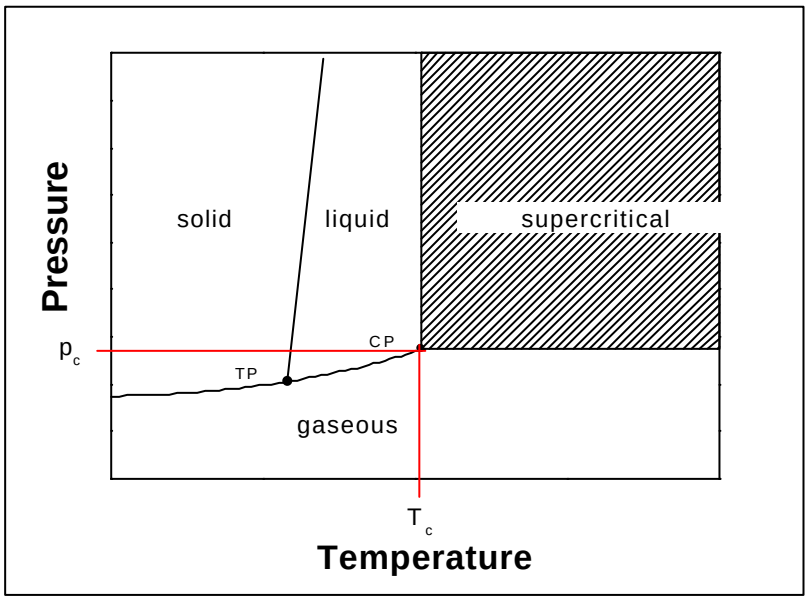

Figure 1: Definition of the supercritical state of a pure component

Water has characteristically high critical values, which are T_c = 647 K and p_c = 22.1 MPa, respectively. With regard to the nomenclature, one refers to the near-critical region as the region which extends all around the critical point, whereas the expression “subcritical” denotes the nonsupercritical state. Depending on which property is below the critical value, fluids whose pressure is below the critical pressure are called subcritical gases, while fluids whose temperature is below the critical temperature are referred to as subcritical liquids [2]. The different areas in the vicinity of the critical point are illustrated in Figure 2.

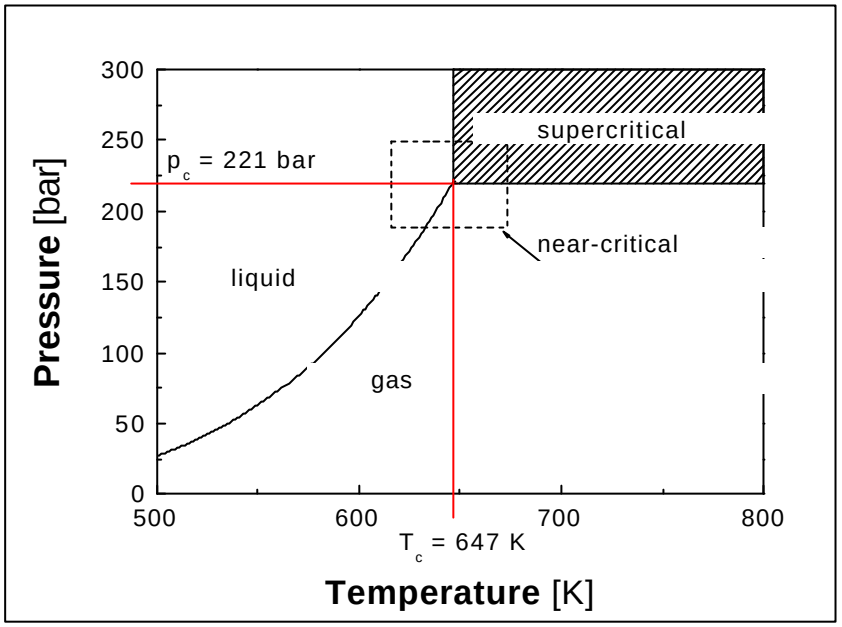

Figure 2: p-T-diagram of water at elevated temperatures and pressures

However, there is no precise definition as where the near-critical region is located. In general, the near-critical condition is referred to as the region in which high gradients in the physico-chemical properties of the substances are observed.

2.2 Properties of near-critical water

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 [3] leads 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 dissociation constant

of water K_W drastically increases from a value of 10^{-14} at ambient conditions to 10^{-11} at subcritical temperatures [4], while at supercritical conditions the ion dissociation constant decreases to values down to 10^{-23}. As a result of this drastic change in the near-critical region, many ionic reactions pathways, e.g. acid and base catalyzed hydrolysis reactions, exhibit a maximum at subcritical temperatures and show a minimum at supercritical conditions.
Beside the dielectric constant and the ion dissociation constant, the fluid density has an important effect on the reaction by influencing strongly the reaction mechanism. In general ionic reaction pathways are favored at higher water densities, whereas the lower densities at supercritical temperatures lead to free radical reaction mechanisms being the preferred reaction pathways.

Due to these unique features, near-critical water serves as an excellent reaction medium and is a highly attractive supplement to biological treatment methods, especially when hardly biodegradable substances like cellulose or related compounds are involved. Near-critical water offers the possibility of controlling and influencing the degradation product distribution by adjusting the operating parameters. In the near-critical region high gradients of the physico-chemical properties with respect to the system pressure and temperature are encountered, thus allowing to change the water properties over a wide range of conditions by slightly varying operating temperature or pressure.

3 Materials and Methods

3.1 Experimental Apparatus

Figure 3 shows a sketch of the experimental apparatus.

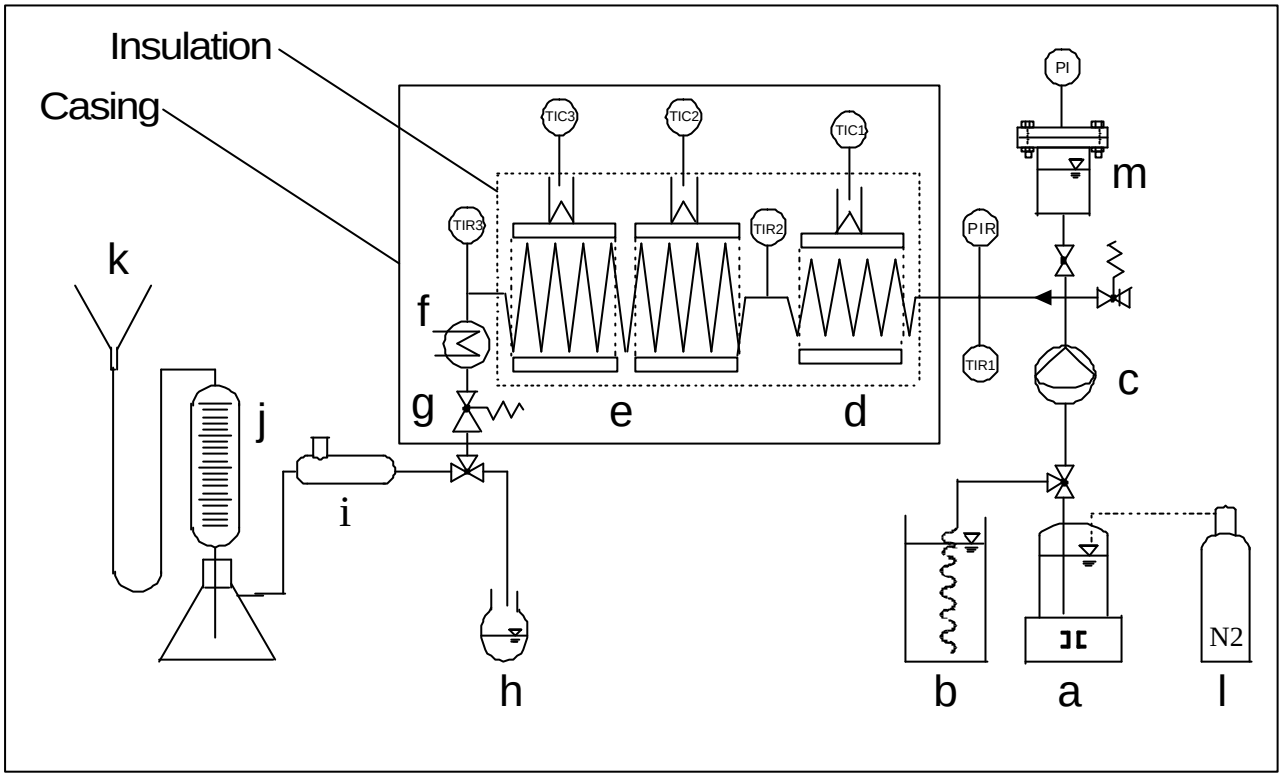

Figure 3: Sketch of the experimental apparatus; *a* feed supply vessel, *b* water storage tank, *c* feed pump, *d* preheater, *e* reactor, *f* effluent cooler; *g* pressure regulator, *h* glass flask, *i* gas mouse, *j* burette, *k* compensator reservoir, *l* compressed gas cylinder, *m* buffer vessel

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 the cooler, expansion valve, and the effluent collection system, respectively. The high pressure reaction unit is designed as a tubular reactor made of high temperature resistant steel (1.4404). The tubular reactor, made of the coiled high pressure piping (o.d. = 0.25 ”, i.d. = 0.125 ”), has an internal volume of V_R = 50 ml and is capable of withstanding operating pressures up to 30 MPa and temperatures up to 673 K. Before entering the reaction unit the feed suspension is preheated in an upstream coil, which has an inner volume of V_{Pre} = 38 ml and is made of the same piping material as the reactor. The preheater and the reaction pipe are electrically heated by means of three heating jackets, which can be adjusted separately by a 2kW temperature control system (Horst HT-60 controller). In order to decrease the heat losses to the surroundings the complete high temperature section of the apparatus is thermally insulated.

The feed suspension is fed from a 2 l closed glass flask covered with a plastic layer. The feed is agitated through a magnetic stirrer to prevent the particulate matter from settling, thus

ensuring a homogeneous feed suspension throughout the vessel. In order to secure that no oxygen re-dissolves in the degasified water the feed suspension is put under a nitrogen atmosphere. This is accomplished by slightly pressurizing the flask with nitrogen gas that flows into the vessel through a hose connected to a compressed gas cylinder. The feed suspension containing the particulate matter is fed into the system by means of a high pressure membrane pump equipped with double ball valves at the suction and the discharge side (LEWA EK1/V metering pump). This redundant double ball configuration serves the purpose of ensuring a reliable operation of the pump even if particles get trapped between one of the balls and its respective seat. In such a case the second ball-seat pair is to secure the closure of the valve.

The water storage tank contains pure demineralized water and fulfils the function of the water supply until the desired operating conditions are reached and the system works at steady state conditions in terms of temperature, pressure, and flow rate. The feed suspension is then introduced into the system by adjusting the position of the three-way valve in the suction line.

Leaving the membrane pump the influent passes a temperature and pressure measuring point and enters the preheater and the subsequent reaction coil. Afterwards the reactor effluent is immediately cooled down by passing a double pipe heat exchanger supplied with tap water as the cooling medium, thus rapidly terminating the reaction. The effluent then passes a pressure regulator valve where it is expanded to ambient pressure. The system pressure is set by adjusting the load of the spring in the regulator valve. The liquid as well as the gaseous effluents are subsequently processed to the effluent collection and measurement system.

The liquid effluents are collected in glass flasks and subjected to the analytical methods which are described in section 3.3 in detail. In order to measure the volumetric gas production as well as the product gas composition a burette system combined with a cylindrical glass vessel equipped with a septum is installed. At the beginning of the gas measurement the effluents flow in an upward direction through the glass vessel (V = 25 ml), which is also known as a gas mouse. This procedure leads to the displacement of any air initially present in the cylindrical shell by the effluents. Afterwards the cylinder is rotated into a horizontal position and gas produced in the course of the reaction is trapped in the upper part of the shell. A flexible hose connecting the gas mouse and the burette serves as a siphon, hereby preventing air from flowing back into the gas mouse and contaminating the product gases. Gas samples can be taken with a gas tight syringe (model Hamilton gas tight, V_{syr} = 1000 µl) and are immediately injected into the gas chromatograph described in section 3.5. The total volume of the effluents entering the system within a certain time can be determined by reading the difference in the liquid level in the burette, which is connected to a compensator reservoir with adjustable vertical position in order to equalize the pressure within the system to ambient pressure.

The system pressure is measured by a pressure transducer; temperatures are measured with high temperature resistant NiCrNi-thermocouples which are welded into pipes and are

inserted into the system by means of tees. Both pressure and temperatures are constantly measured and recorded at the positions indicated in Figure 3. In order to minimize pressure fluctuations, which are due to the operation of the discharge valve of the pump and the opening of the pressure regulator, the system is attached to a buffer vessel which has an internal volume of V_{in} = 3.5 l and which is filled with a nitrogen headspace.
The flow through the system is measured gravimetrically by weighing the feed and the sample vessels with a laboratory scale, since mass flow meters that are based on the Coriolis-principle bear the risk of clogging when suspensions containing larger particles are discharged through their internal tubes.
For the sake of safety all parts of the apparatus that are set under elevated temperatures are completely cased. In order to prevent an excessive pressure build-up within the system the apparatus is equipped with a pressure relief valve.

The experimental set-up described above can be operated in a pressure range up to 30 MPa and allows to cover temperatures up to 400°C. Although according to the manufacturer the membrane pump exhibits a pressure firm characteristic, the system pressure shows a noticeable influence on the rate of metered flow. At an operating pressure of 25 MPa the maximum flow is in the range of 4 l/h.

3.2 Substrate preparation

Table 1 shows the substances used in the experiments so far.

	Source	Dry matter content [% w/w]
Cellulose	Merck AG, Darmstadt	
Wheat straw	Local farmer	~ 94.5
Cabbage	Market	~ 9.7
Soya waste	Oil-mill	~ 91.1
Algae (Spirulina)	BlueBioTech GmbH	~ 95.5

Table 1: Substances employed as substrate so far

The dry matter content listed in the third row of Table 1 is determined by filling substrate samples in evaporation bowls and drying the samples at a temperature of 60°C in a desiccator cabinet. The water content of the substrate material is determined by measuring the weight loss of the respective sample after a drying period of 2 days.
Microcristalline cellulose was purchased from Merck AG and is used as received. The other components are ingredients of the ESA substrate as agreed on at the Progress Meeting in Gent and were obtained from the sources stated in Table 1. Except for cellulose and the spirulina

organisms, which exhibit an appropriate particle size, all components have to undergo a multi-step conditioning process before they can be introduced into the experimental apparatus.

The wheat straw proved to be the component most difficult to grind. In order to obtain a sufficient size reduction the straw is successively introduced to a rotary cutter and a centrifugal impact mill. Although in theory only particles smaller than $d_p = 250$ µm are allowed to pass the strainer used in the mill, also fibrous particles whose largest physical dimension is greater than the average mesh size are found in the grinding stock. Therefore the straw is subsequently processed in a coffee mill.

The soya waste is received in pellet shaped agglomerates whose binding strength can be overcome in a coffee mill. The cabbage is treated with a grater to yield a pulp.

Following these dry size reduction operations the substrate is treated with a homogenizer (model Heidolph DIAX 900) in order to further decrease the particle size. The dry matter content of the resulting suspension is adjusted to the desired experimental conditions by adding demineralized water.

The feed water is provided by the demineralized water-supply system of the Technical University. It is degasified in an ultrasonic water bath and added to the substrate at a predetermined ratio. Afterwards it is immediately filled in the feed supply flask and put under a nitrogen headspace according to the method described in section 3.1.

3.3 Liquid analysis

3.3.1 HPLC analysis of main degradation products

The HPLC system described below serves the purpose of identifying the main degradation products and determining their respective concentrations.

Technical Specifications	HPLC	Macherey Nagel, Nucleogel®Sugar
	Column Type	Packed Column; L = 300 mm, i.d. = 7.8 mm Packing material: Cation exchange polymer
	Guard Column Type	Packed Column; L = 21 mm, i.d. = 4 mm
	Detector Type	Refractive Index
Operating Conditions	Eluent	Distilled Water
	Eluent Flow	0.5 ml/min
	Oven Temperature	72°C, isothermal

Table 2: Specifications of the initial HPLC set-up

Pure demineralized and degasified water serves as the eluent and is pumped with a piston pump (Merck-Hitachi-L7100) at a flow rate of 0.5 ml/min into a 6 way injection valve (Rheodyne 7725i). Small amounts of the liquid samples are injected (injection volume 20 µl) into the eluent flow and separated with a Nucleogel®Sugar column packed with a cation exchange polymer. This packing material is especially designed to separate mono- and disaccharides and the degradation products thereof. The components are identified with a refractive index detector (RI-IV LCD Analytical) and are quantified by injecting standard solutions at different concentrations. The operating conditions stated in Table 2 have proven to yield good separation results in the characterization of degradation products of starch experiments, which were performed in the Department for Thermal Separation Processes in the past.

Unfortunately, the differential pressure across the column showed a steep increase from about 70 bar to 170 bar after a few injections, such that only samples of the first test runs could be analyzed. The number of standard solutions injected into the system does not suffice to determine the concentration of the components detected in the samples, such that no quantitative analysis can be conducted on the basis of these chromatograms.

There are two possible sources for the sudden increase in operating pressure, which renders this column useless to further analytical evaluations. One reason may be the deposition of solid particles on the packing material within the column. However, there are a number of aspects contradicting this explanation. One aspect is the careful sample preparation. Liquid samples were first filtrated by means of microfilters with a mean pore size of 0.2 µm and subjected to a centrifuge at 13.000 rpm afterwards. This procedure and the use of a specially designed guard column filled with the same packing material as the HPLC column let it seem very unlikely that particle deposition is responsible for the drastic increase in differential pressure. In addition, neither backwashing the column with acetonitrile nor using solutions at severe acidic and alkaline conditions resulted in an improvement of the column performance in terms of a decrease in operating pressure. Therefore the sudden, irreversible increase in pressure is probably due to a failure of the polymer matrix in the HPLC column, which generally is a result of the limited lifetime and therewith limited total number of injections. Since this break down necessitates the replacement of the HPLC column, the liquid effluent samples are currently analyzed with an alternative HPLC set-up in order to identify the main liquid degradation products.

3.3.2 Determination of DOC

The amount of dissolved organic carbon in the feed and effluent samples is determined with a TOC analyzer (model Elementar “HighTOC + TN_b”). Liquid samples are filtrated through 0.45 µm filter units and are injected in the fully automatic analyzer, where they are

completely oxidized. The carbon content is determined by measuring the resulting CO_2 concentration with an IR detector.

3.4 Solid residue analysis

In order to determine the conversion rate on a dry matter basis the weight fraction of the solid residues is evaluated. For this purpose liquid effluent samples can be subjected to two different treatment methods. Whole effluent samples of about 20 ml are filled in evaporation bowls and kept in a desiccator cabinet for two days at 60°C. This way the weight fraction of the solid matter can be determined by measuring the weight of the bowl with and without the solid material as well as the weight of the bowl containing the whole effluent sample. The other method is to run effluent samples through one way filter units (Schleicher&Schuell) with a mean pore size of 0.45 µm and determining the amount of solid residue trapped in the filter by determining the dry weight difference of the filter unit.

3.5 Gas composition analysis

The composition of the gas phase is analyzed with a gas chromatograph (model Perkin Elmer 8500) equipped with a heat conductivity detector (HCD). Gas samples are taken from the gas mouse with a gas tight syringe and are immediately injected in the GC operated in off-line mode. The technical details of the gas chromatograph are depicted in Table 3 below.

Technical Specifications	Gas Chromatograph Model	Perkin Elmer 8500
	Column Type	Packed Column; L = 2m, i.d. = 2mm Packing material: Propak Q 100-120 mesh
	Detector Type	Heat Conductivity Detector
Operating Conditions	Carrier Gas	Helium 4.6
	Carrier Flow	15 ml/min
	Oven Temperature	120°C, isothermal
	Injector Temperature	120°C
	Detector Temperature	120°C
	Injection Volume	400 µl

Table 3: Technical specifications and mode of operation of GC analysis

Helium (purchased from Westfalen AG) was chosen as the carrier gas since its thermal conductivity is distinctly different from those of most other gaseous components under the operating conditions stated above, thus allowing the identification of main constituents like carbon dioxide, nitrogen, and methane. Peak identification was accomplished by injecting

standard samples of the pure components and measuring their retention times. The quantitative analysis of the effluent gas composition is done according to the area percentage method, which leads to the determination of the quantitative ratio of the components instead of absolute concentration values.

4 Results and Discussion

4.1 Experimental Conditions

Table 4 shows the experimental conditions of the first test runs.

Number	Substrate	T [K]	P [MPa]	τ [sec]	C_0 [% w/w]
1	Cellulose	647	23.4	28	0.49
2	Cellulose	619	23.9	36	0.53
3	Cellulose	640	24.1	38	0.49
4	Wheat straw	639	23.5	59	0.40
5	Wheat straw	633	23.0	52	0.39
6	ESA substrate: w_{straw} = 27.7 % $w_{cabbage}$ = 27.3 % w_{soya} = 30.4 % w_{algae} = 12.6 %	639	23.2	29	0.89

Table 4: Experimental conditions of first runs; τ: mean residence time, C_0: initial solid concentration

The temperatures and pressures stated in the second and third row are the respective mean values during the experiment. Due to the low substrate concentrations, the mean residence time was calculated under the assumption that the feed density can be approximated by the density of pure water:

$$\tau = \frac{V_R}{\dot{V}_{(T,p)}} \approx \frac{V_R}{\dot{m}} \cdot \rho_{H_2O,(T,p)}$$

Values for pure water densities were taken from [5]. The initial solid concentrations C_0 are given on a dry matter basis, taking into account the respective water contents as stated in Table 1. As can be inferred from the table, the dry matter content of the feed suspension so far is below the value for the current MELISSA feed. This is due to the difficulties encountered when pumping wheat straw with the configuration described in section 3.1. As a result of the

fibrous structure of the straw, particles may be trapped in the inlet and outlet valves, thus causing a sudden pressure decrease. Figure 4 illustrates this problem by means of a course of pressure.

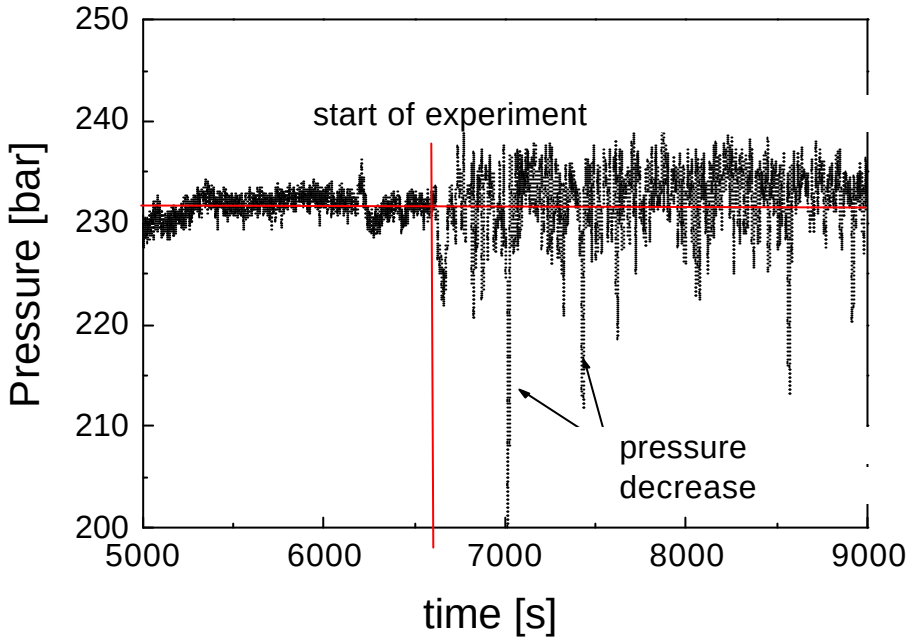

Figure 4: Course of pressure for an experiment using the ESA substrate as feed

The start of solid feeding is marked by an increase in pressure fluctuations. At the points indicated by the arrows the system pressure abruptly decreased, which probably is due to the fact that the valves did not perfectly close as a result of clogging. Therefore, higher solid concentrations might lead to a decrease in reliability by increasing the risk of failure of the pump. The determination of the maximum solid concentrations and the possibility of influencing it by decreasing the particle size are to be investigated in future experiments.

4.2 Particulate matter conversion and DOC analysis

In order to determine the degree of liquefaction for the different substrates the change in the dissolved organic carbon content and the conversion of the particulate matter was evaluated. Table 5 shows the results of the liquefaction experiments in terms of the change in total organic carbon in the liquid phase and the reduction of the weight fraction of particulate material.

Number	DOC_0 [mg/L]	DOC [mg/L]	f [%]	pH
1	75	1216	~ 99	2.99
2		1802	~ 99	2.76
3		899	~ 99 (92)	2.94
4	91	456	~ 96	3.74
5		865	~ 91 (64)	3.59
6	741	2558	~ 90	3.97

Table 5: Results of liquefaction experiments; DOC_0: initial dissolved organic carbon, DOC: effluent dissolved organic carbon; f: particulate matter conversion factor; pH: effluent pH-value

Comparing the initial organic carbon DOC_0 and the effluent carbon DOC of the liquid phase the amount of dissolved organic carbon shows a steep increase for all experiments. This is due to the fact that insoluble substrate ingredients were converted into water soluble components in the course of the reaction, meaning that particulate matter become liquefied as a result of the hydrothermal treatment.

The particulate matter conversion factor f is defined as the decrease in the solid concentration divided by the initial concentration C_0 in the feed suspension

$$f = \frac{C_0 - C}{C_0}$$

where the solid concentrations are calculated on a dry matter basis. The values given in brackets were determined by evaporating total liquid effluent samples whereas all other solid conversions were quantified by drying the residues on 0.45 µm filter units as described in section 3.4. It can be inferred from the table that the two methods exhibit a significant difference in the determination of the solid concentration. This can either be due to a high fraction of very fine components which were able to pass the filter unit or more likely be due to the reformation of solid matter. The fact that in initially apparently clear filtrate the precipitation of very fine solid material was observed, supports the second assumption.

As can be inferred from Table 5, the pH-value exhibits a significant drop for all experiments. This decrease is probably due to the formation of organic acids like formic and acetic acid during the course of the reaction.

All experimental runs show very high conversions with respect to the particulate matter within residence times of less than a minute. In the cellulose experiments a close to complete liquefaction of the solid material was observed, while in case of wheat straw as the substrate a residual amount of particulate matter was found in the effluent. Employing the ESA substrate without the fecal material yielded a particulate matter conversion of 90 % within a residence time of about half a minute at the conditions specified in Table 4.

4.3 Gas phase analysis

Except for nitrogen gas, which is probably introduced into the system by mixing the feed suspension under the nitrogen atmosphere, only carbon dioxide was detected in the experiments so far. However, the amount of gas produced in the reactions was very low compared to the total carbon fed to the reactor. Depending upon the operating conditions, the total measured gas flow, in terms of volumetric gas production with respect to the amount of carbon fed to the reactor, was in the range of 50-70 ml/g_{Carbon}. Evaluation of the volumetric gas production and the determination of the percentage of carbon dioxide by GC analysis lead to the result that only about 1 percent of the carbon initially present in the cellulose is converted into the gas phase. Thus it appears that the particulate matter in the substrate is mainly liquefied.

5 Summary/Outlook

5.1 Current State

Preliminary experiments using cellulose as a model compound for plant biomass have been conducted. Wheat straw as one of the main constituents of the non-edible plant material was fed to the reactor. A first test run employing the ESA-substrate as defined at the progress meeting in Gent omitting the fecal material was conducted. The experimental and the analytical procedures are established, such that the tubular reactor for the near-critical treatment of the ESA-substrate is operational.

The preliminary experiments show a strong increase of the DOC of the liquid phase combined with a drastic decrease of the particulate matter content. Only carbon dioxide could be identified as product gas. These results prove that the near-critical treatment of the biomass is a suitable method to achieve very high conversions at residence times of less than one minute and that the solid material is primarily liquefied (proof of principle). A detailed analysis of the liquid effluents in terms of the identification of the main degradation products and their quantities is expected to be available from the analytical laboratory soon.

In order to secure that the substances produced in the course of the reaction do not exhibit a detrimental effect on the organisms in the biological degradation compartments, liquid effluent samples need to be fed to a methanogenesis unit.

5.2 Outlook

Having shown the feasibility of the hydrothermal treatment of the ESA-substrate the tasks to be performed next will be the substrate exchange and the feeding of the effluents to the methanogenic test reactor of Partner 3. Beside this validation of the non-toxicity of the

reaction products, the reactor performance is to be optimized with respect to the liquefaction of the particulate material as described in the second work package (W.P.REF. 4.200).

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