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on the MAP-Project

"A Total Converting and Biosafe Liquefaction Compartment for MELISSA"

Work Package 4.300: 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 for Thermal Separation Processes, Technical University of Hamburg-Harburg. Beginning with a brief outline of the objectives of the third stage of the project, this paper covers the description of the experimental approach, including the presentation of necessary modifications to the experimental apparatus, the materials employed in the experiments, and the analytical procedures used to characterize the influents and effluents. This part is followed by a section presenting and discussing the latest result of the hydrothermal treatment at subcritical water conditions. In this context, the degrees of conversion, the material balances, and a preliminary approximation of the energy requirements for the mechanical pre-treatment are given. The technical note concludes with a summary of the tasks completed in accordance with the work package description (WP. Ref. 4.300) and an outlook of the activities for the next stage of the project.

2 Objectives

The feasibility of a hydrothermal treatment for the rapid conversion of biomass at subcritical water conditions has been shown in the preceding stages of the project. Based on these results, it was decided at the 2nd Progress Meeting in Barcelona that the indigestible solid residues of the methanogenic reactor (Partner 1) were to be subjected to a hydrothermal post-treatment. This approach employing a physico-chemical treatment is aiming at a close to complete conversion in the overall scheme by liquefying the recalcitrant matter, which is not further degradable by biological means. In order to investigate the performance of such a set-up, first closed loop experiments were to be conducted by exchanging reactor effluents between Partner 1 and Partner 4. This way, the degree of conversion achievable by a subcritical water treatment and the biodegradability of the effluents thereof were to be studied. Based on these results, the material balances in terms of carbon and nitrogen were to be calculated. One preliminary test using carbon dioxide to decrease the pH-value and promote acid catalysed cleavage reactions was also performed.

In parallel, the model studies using pure substances were continued. The materials employed in these experiments were cellulose as the most abundant biopolymer and the most important constituent of plant biomass and bovine serum albumin as a protein. The objectives of these experiments were to gain more information about the product formation and the contribution of polypeptides in the effluents of the hydrothermal reactor at different operating conditions and residence times.

In addition, issues like the development of an appropriate dry size reduction procedure and the energy requirement thereof were to be discussed. The fact that the thermal treatment imposes an additional hygienic barrier on the system was to be proven.

3 Materials and Methods

3.1 Modifications of the experimental apparatus

So far all experiments have been conducted with one single high pressure membrane pump delivering the feed suspension into the tubular reactor. This set-up bears the disadvantage that the heating time required to adjust the temperature to the desired level is in the same range as the total residence time, since the energy cannot be introduced into the system instantaneously. This led to a noticeable temperature difference between the inlet and the outlet of the reactor, such that the operating conditions were not isothermal and the true residence time could not accurately be determined. Therefore a second membrane pump delivering pure water was coupled to the system. By preheating the water stream and mixing it with the moderately heated feed flow directly before the reaction coil, the temperature profile along the reactor could be decreased dramatically. A careful choice of flow rates and their respective temperatures results in an average temperature difference in the range of one to two degrees, thus ensuring isothermal conditions and a well defined residence time. Figure 1 shows a sketch of the modified experimental set-up and an exemplary course of temperature obtained with the new configuration.

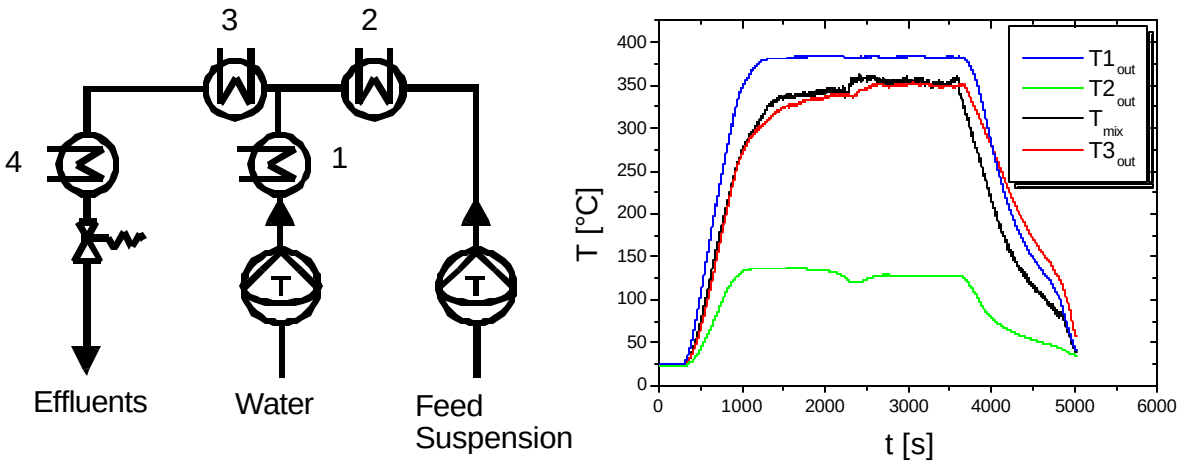

Figure 1: Modified experimental set-up (left) and respective course of temperature (right)

The course of temperature depicts that the temperature at the mixing point directly at the reactor inlet (T_{mix}) and the temperature at the reactor outlet ($T_{3,out}$) are nearly identical during the experiment, while the feed is only moderately heated prior to the mixing ($T_{2,out}$).

3.2 Substrates/Substrate preparation

The solid residues from the methanogenic bioreactor of Partner 1 were received in the form of dry agglomerates. Immediately before the experiment they were subjected to a mechanical pre-treatment in a cutting mill and afterwards suspended in pure demineralised water.

Cellulose was obtained as micro-crystalline powder from Merck. Bovine serum albumine was also purchased from Merck. These materials did not require any pre-treatment but could be used as received.

As compared to the multi-step mechanical pre-treatment discussed in the last technical note, the preparation of the solid residues from Partner 1 was facilitated by the acquisition of a laboratory scale cutting mill. Figure 2 shows a photograph of the front side with the lid opened.

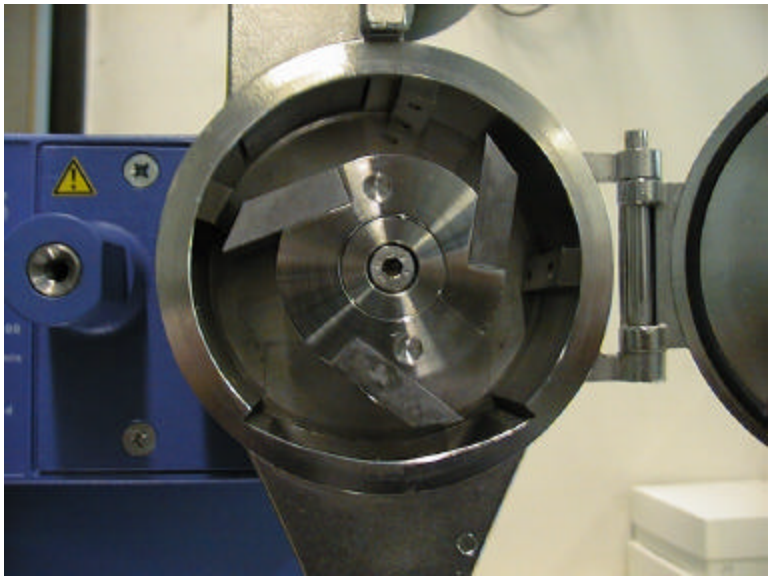

Figure 2: Front view of the newly acquired cutting mill

Size reduction in this device is performed by cutting particles which are between the sharp-edged knives mounted on the rotor and the counterparts fixed at the body of the mill. The mill is charged from the top and the ground stock is discharged at the bottom after passing a sieve. By consecutively using sieves with 1000µm and 250µm mesh size the solid residues could

conveniently be broken down to an acceptable particle size. However, there was one portion of grain-like material which could not be cut down easily but plugged the mesh of the 250µm sieve. This problem was overcome by separating this material and treating it in a coffee mill, where it was reduced to smaller pieces by hitting a sharp-edged rotor.

3.3 Analytical procedures

Liquid effluents of the experiments using the solid residues from Gent as substrate were characterized with respect to sum parameters. The determination of the chemical oxygen demand (COD), the amount of ammonia nitrogen (NH_4-N) and nitrogen in the nitrate form (NO_3-N) was accomplished by using standardized cuvette tests (Dr. Lange). The concentration of total carbon (TC), total organic carbon (TOC), and total nitrogen (TN) of the effluents was determined by burning samples in a TOC-analyser (Elementar "HighTOC + TN_b"). In addition, solid samples of the residues were analysed with respect to their carbon, nitrogen and sulphur content by means of a CNS-analyser (Leco-CNS-2000-Analyser).

For the experiments using cellulose and bovine serum albumine the identification of the main degradation products was achieved by HPLC-analysis. The set-up and the mode of operation of the HPLC-system for sugar analysis have been described previously. The separation and detection of amino acids was accomplished by a RP-HPLC-system with derivatization of the amino acids prior to the separation in the column and fluorescence detection of the derivatives. The main specifications for this system are summarized in Table 1.

Technical Specifications	HPLC	Merck, Superspher 4 RP18
	Column Type	Packed Column; L = 250 mm, i.d. = 4 mm
	Detector	Fluorescence, 340/420nm
Operating Conditions	Eluent	A: Sodium acetate; B: Methanol
	Eluent Flow	0.7 ml/min
	Eluent Mode	Isocratic, Gradient
	Oven Temperature	40°C, Isothermal

Table 1: Specifications of the HPLC system used for the analysis of amino acids

The effluents were treated with borate buffer and protein precipitant and were centrifuged at 16.000g. Afterwards the derivatization was performed with ortho-Phtaldialdehyde (OPA) and 15µl of the resulting reaction mixture were injected into the column.

Peak identification and quantification of the amino acids are accomplished by injecting external standards with known concentration of the amino acids. By injecting β-Alanin, which does not belong to the group of proteinogenic amino acids, as an internal standard, the peak

area ratio of sample and standard solution can be determined, thus allowing to determine the amino acids concentration very accurately.
This method is capable of detecting and quantifying all proteinogenic amino acids.

4 Results and discussion

4.1 Liquefaction of ESA-substrate

4.1.1 Degree of liquefaction based on the carbon balance

The results of the liquefaction experiments in terms of the carbon balance are summarised in Table 2.

No	T [°C]	P [bar]	τ [s]	$C_{sol.out}/C_{in}$ [%]
1	360	240	25.1	73.9
2	366	238	39.7	56.4
3	360	233	38.8	57.1
4	301	250	87.2	44.8
5	319	247	45.2	58.7
6	406	264	> 35	57.2

Table 2: Conversion of Gent residues in terms of carbon

All experiments were conducted with initial solid concentrations of about 0.5 weight percent on a dry matter basis. The experimental temperature, pressure, and the residence time calculated on the average of inlet and outlet temperature are stated. The values reported in column 5 are the ratios of dissolved effluent carbon to total influent carbon. The dissolved carbon was determined experimentally by means of a TOC-analyser. The total influent carbon was calculated on the basis of the influent solid concentration and the carbon content of the solid material, which was determined by composition analysis with a CNS-analyser. The ratio of dissolved carbon to total influent carbon serves as a measure to evaluate the degree of liquefaction based on the carbon balance.
As can be read from the values, the experiments were conducted in a relatively narrow pressure range, such that the influence of the experimental temperature and the residence time on the conversion to soluble carbon components can be studied. Comparing the first two runs , the degrees of conversion are surprisingly inconsistent, since the first run yields a comparatively high conversion though temperature and residence time were lower than for the second one. This may only be explained by the fact that for the first run the solid material was

taken from the first batch of reactor residues from Gent while all other runs were conducted with residues from the second batch. As the solid material was subjected to no analysis other than the composition in terms of carbon, nitrogen, and sulphur, there is no information available about the different components in the substrate. For this purpose, the van Soest-method needs to be employed to characterise the composition in terms of cellulose, polyose, and lignin. Based on the experimental runs it seems that the first batch of residues from Gent was containing more readily degradable components than the second one.

The second and third run were conducted at nearly identical experimental conditions in order to check the reproducibility of the experiments. Comparing the degrees of liquefaction it can be concluded that the results differ less than 1 % with respect to the conversion and therefore are in very good agreement. The fourth run was performed at a much lower temperature of 300°C and yields a significantly lower degree of liquefaction of 45 %, though the residence time of 87 s was much longer than for the other runs.

For the fifth run the conversion into soluble components is essentially the same as for run 2 and 3, although the mean temperature is much lower. This may be explained by the fact that for this particular experiment the temperature at the reactor inlet and outlet exhibited a relatively large deviation, meaning that the outlet temperature was in the same range as for run 2 and 3. This finding points to the assumption that the solid residues contain a certain fraction which cannot easily be liquefied by increasing the residence time within a narrow range at temperatures of about 360°C.

Even an increase in temperature to 406°C, which is well above the critical temperature of pure water, did not result in a higher degree of liquefaction within the residence time employed in the experiments. As a conclusion, about 40 % of the carbon are very difficult to liquefy without a further increase in residence time. To clarify which components do contribute to the non-dissolved carbon, the solid material needs to be analysed be the van Soest- method.

In order to increase the degree of conversion, carbon dioxide was added to the system by which means the pH-value is considerably lowered. The effect of acidification by carbon dioxide on the degree of conversion is described in section 4.1.3.

Plausibility:

In order to check the plausibility, the effluent solid of run 6 was analysed with respect to its carbon content. By determining the solid concentration of the effluent and knowing the carbon content of the solid phase, the contribution of the solid carbon to the total effluent carbon can be calculated directly. Summing up the solid carbon and the dissolved carbon gives about 91 % of the expected total carbon based on the substrate composition and the respective influent concentration. This slight mismatch might be partly explained by carbon converted into the gas-phase.

4.1.2 Calculation of nitrogen mass balance

In order to calculate the nitrogen mass balance for the subcritical degradation unit, the total nitrogen content of the influents and effluents was measured by means of a TOC, TN analyser. In addition, the ammonia nitrogen and nitrate concentrations of the effluents were determined using Dr. Lange cuvette tests. The results of these analyses and the ratio of COD in the liquid phase to the total effluent COD are summarized in Table 3.

No	$COD_{sol.out}$ /COD_{tot} [%]	$N_{sol.out}$ /N_{in} [%]	NH_4-N [mg/l]	NO_3-N [mg/l]	NH_4-N+NO_3-N /$N_{sol.out}$ [%]
1	59.9	n.d.	n.d.	n.d.	n.d.
2	56.7	97.1	38.5	21.1	56.7
3	67.5	92.8	37.0	22.7	62.1
4	67.6	75.7	44.5	25.6	57.0
5	61.7	103.9	41.8	20.6	45.8
6	66.4	110.0	87.5	46.3	55.3

Table 3: Computation of nitrogen balance

The notation of the experimental runs corresponds to the measurements described in section 4.1.1. The calculation of the influent nitrogen concentrations is based on the analysis of the molecular composition of the substrate. The values of the measured soluble nitrogen concentrations of the effluent and the respective ammonia nitrogen and nitrate concentrations of the effluent are reported.

It can be concluded that the degree of liquefaction based on the nitrogen balance is higher than the respective degree based on the carbon balance, which means that nitrogen is more readily converted into soluble components than carbon. Except for run 4, which was conducted at a significantly lower temperature, essentially all nitrogen initially present in the solid phase was converted to water-soluble components in the course of the reaction. Regarding the composition of the water soluble, nitrogen-bearing components, nitrogen in the ammonia and nitrate form amounts to about 60 % of the total nitrogen detected in the liquid phase. This means that there still is a significant amount of unknown species which contribute to the soluble nitrogen. For this reason, additional experiments with bovine serum albumine were conducted in order to clarify if nitrogen bound in polypeptides can be detected at the conditions employed in the experiments.

4.1.3 Acidification by carbon dioxide

Due to the increased solubility of carbon dioxide in water at elevated temperatures and pressures, the addition of carbon dioxide can serve as a means to lower the pH-value without the need of mineral acids. This approach bears the advantage of easily recovering the carbon dioxide in the gas phase, such that additional downstream unit operations like neutralisation and precipitation steps become superfluous. By decreasing the pH many acid catalysed reactions like the hydrolysis of glycosidic and peptide bonds can be greatly accelerated. Figure 3 depicts the pH-value in water saturated with carbon dioxide as a function of temperature at different operating pressures.

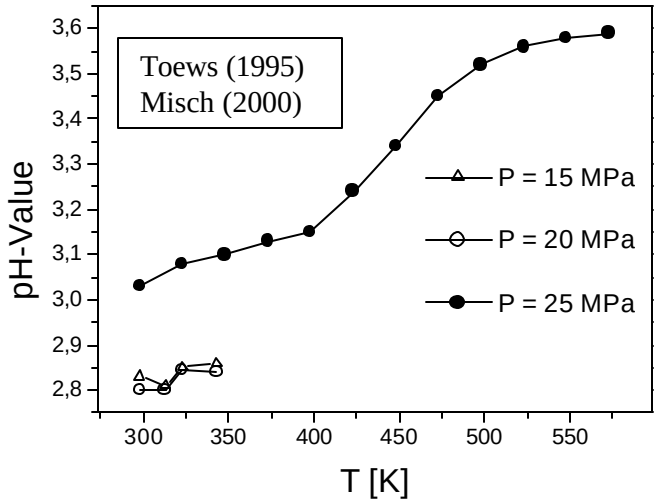

Figure 3: pH-value of aqueous phase saturated with carbon dioxide, taken from [1]

To take advantage of this property, one preliminary experiment adding carbon dioxide to the influent suspension was performed. Carbon dioxide was liquefied by a refrigeration unit and delivered into the system by means of a membrane pump. Solubility data of carbon dioxide in water at high temperatures and pressures were taken from phase equilibrium data in literature [2]. The desired degree of saturation of 50% was achieved by measuring the gravimetric flow rate of the carbon dioxide with a mass flow meter and adjusting the flow rate at the pump to the required level. Table 4 reports the operating conditions and the degree of liquefaction for this experimental run.

CO_2-Saturation	T [°C]	P [bar]	τ [s]	$C_{sol.out}/C_{in}$ [%]
~ 50%	341	238	~ 50	83.4

Table 4: Degree of liquefaction with acidification by carbon dioxide

As can be inferred from this experiment, the ratio of soluble effluent carbon to calculated influent carbon was significantly higher than in case of the non-catalysed experiments at nearly identical conditions. Based on this result, the acidification by carbon dioxide appears as a highly attractive supplementary method to readily convert the most recalcitrant solid matter. Therefore, further experiments are scheduled to elucidate the influence of carbon dioxide in the conversion of biopolymers.

4.2 Cellulose degradation experiments

Cellulose degradation experiments were continued in order to study the liquefaction and the product formation of this most important constituent of plant biomass. As described in the previous technical note, the conversion of cellulose into water-soluble substances based on the carbon balance is close to complete within residence times of less than half a minute at temperatures higher than 300°C (see Figure 4).

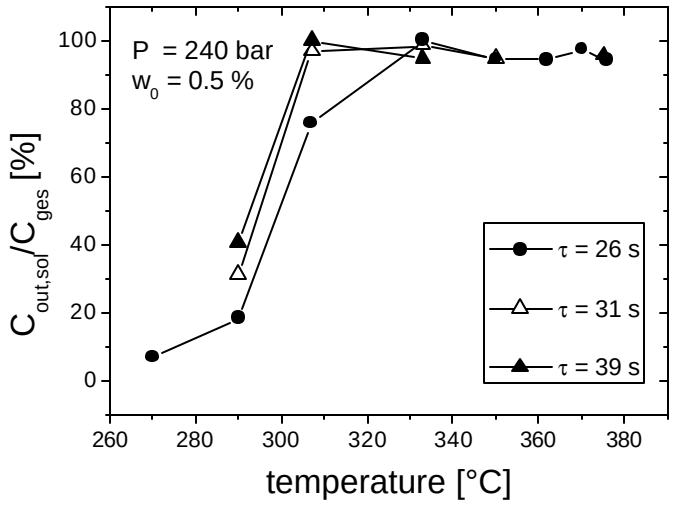

Figure 4: Ratio of soluble carbon to total carbon

The main degradation products at different temperatures and residence times were determined by means of HPLC-analysis. It can be concluded that at temperatures less than 300°C the mono-, di- and oligosaccharides have a major contribution to the soluble carbon, while at higher temperatures saccharides are degraded by consecutive reactions and secondary reaction products like hydroxymethylfurfural, levoglucosan, and acetic acid are produced. The course of concentrations of glucose, fructose, maltose, and raffinose versus residence time at different temperatures is reported in Figure 5.

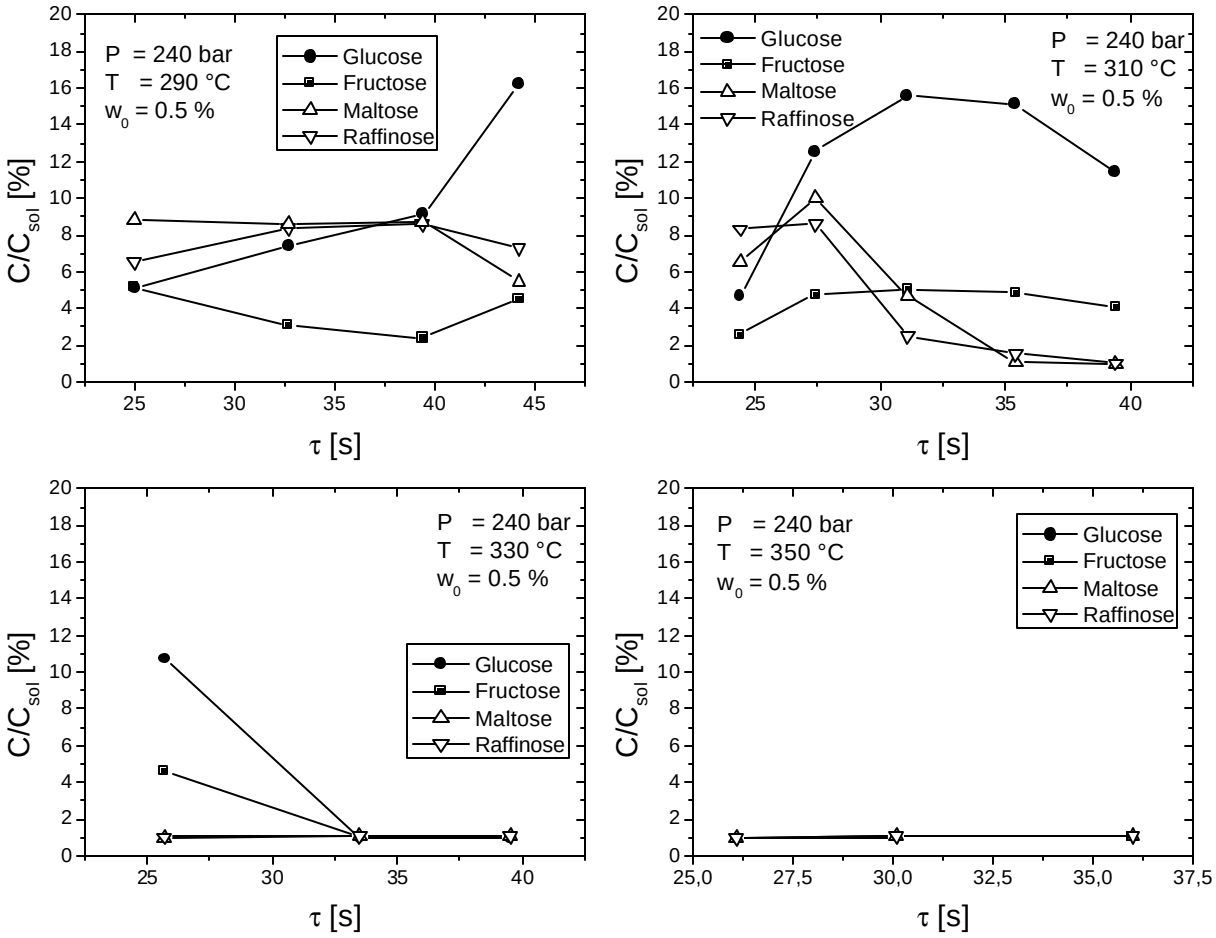

Figure 5: Ratio of carbon bound in saccharides to total soluble carbon

While at a temperature of 290°C the glucose concentration shows an increase with time, the levels of fructose, maltose, and raffinose concentration stay essentially constant. In contrast, the concentrations at 310°C exhibit markedly different profiles. The glucose concentration shows a steeper increase after shorter residence times as compared to the experiment at 290°C. Afterwards it passes a maximum with a subsequent decrease. The maltose and raffinose concentrations start to decrease at residence times of 25 s to 30 s and they subsequently fall below the quantification level. Regarding the respective degrees of conversion, this behaviour may be explained by the fact that the cellulose is completely hydrolysed to water soluble substances such that no more di- and oligosaccharides are produced but consumed for the formation of monosaccharides and degradation products thereof. The formation of secondary products can serve as an explanation for the drop in glucose concentration with increasing residence time.

This behaviour is even more pronounced at temperatures of 330°C and 350°C. While at 330°C the concentrations of glucose and fructose decline after short residence times, no glucose and fructose could be detected at an experimental temperature of 350°C.

4.3 Protein degradation experiments

Protein degradation experiments were conducted in order to determine the degree of hydrolysis of polypeptides at operating conditions. This study serves the purpose of clarifying if organically bound nitrogen in form of amino-groups has a significant contribution to the still unidentified portion of soluble nitrogen. Furthermore, the destruction of polypeptides and the occurrence of free amino acids may be regarded as evidence that the reactor effluents are sterile.

Bovine serum albumine was employed in the experimental runs since this protein exhibits a well-defined and known structure and has a limited solubility in water. The experimental conditions covered temperatures from 250°C up to 350°C at a constant pressure of 248 bar and residence times from 58 s to 129 s. The effluents were subjected to the aforementioned amino acid analysis. Figure 6 shows a chromatogram obtained from one of the experimental runs.

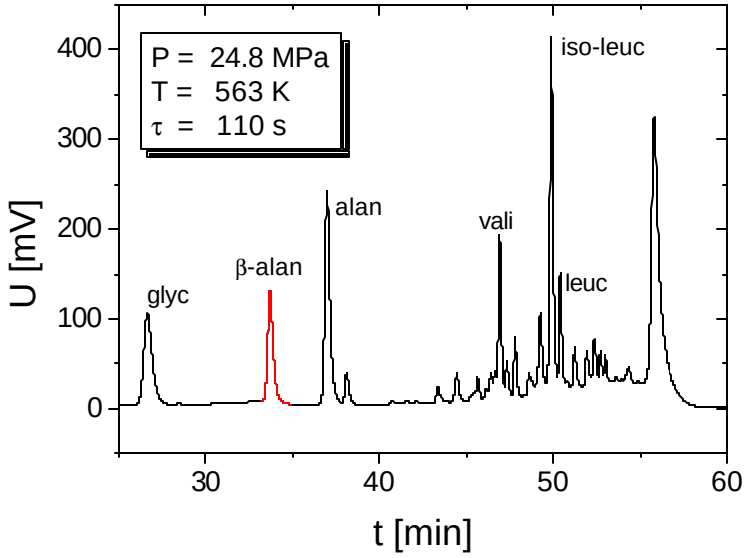

Figure 6: Chromatogram obtained from HPLC -analysis of reactor effluents

The chromatogram reports the existence of free amino acids at a temperature of 290°C and a residence time of 110 s. The red marked peak is caused by β-alanin as the internal standard. Especially glycin, alanin, histidin, phenylalanin, valin, iso-leucin and tyrosin could be detected in significant concentrations. Comparing the actual concentrations with the

theoretically possible ones from the albumine sequence, the yield of these amino acids exceeded 10 %. The yield of iso-leucin was about 60 %, the yields of alanin and glycin were 40 % and 45 %, respectively.

In contrast, at a temperature of 350°C and a residence time of 85 s no free amino acids except for iso-leucin and phenylalanin could be detected in significant amounts, which is probably due to the decomposition of free amino acids at increasingly high temperatures.

In order to further study the degree of albumine degradation, the reactor effluents were subjected to a complete hydrolysis with hydrochloric acid for 16 h at a temperature of 110°C. In this way the amount of the different amino acids in the hydrolysates can be compared to the amounts in the influent, which are calculated from the albumine sequence. By subtracting the amounts of free amino acids in the effluents from the respective amounts in the hydrolysates, the amount of the different amino acids bound in peptides can be determined and related to the original amount in the influent. The ratio of free amino acid in the effluents and the amino acid in the hydrolysates with respect to the calculated influent amino acid content is depicted in Figure 7 for alanin and phenylalanin.

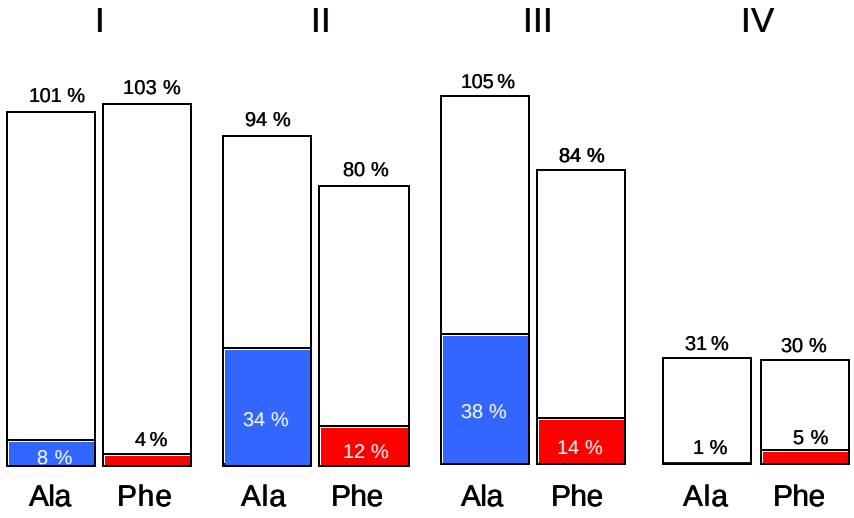

Figure 7: Amount of amino acid in hydrolysate and amount of amino acid in effluent with respect to the influent amount for Alanin (Ala) und Phenylalanin (Phe): Conditions: P = 250 bar; I: T = 250°C, t = 129 s; II: T = 290°C, t = 65 s; III: T = 290°C, t = 111 s; IV: T = 350°C, t = 85 s

The results show that the concentration of alanin in the hydrolysate equals the calculated alanin concentration based on the albumine sequence up to 290°C, while for the experimental run at 350°C a significant decrease of the alanin concentration could be observed. This behaviour can probably be attributed to the fact that alanin is not thermally stable at such temperatures and decomposes due to secondary reactions. This assumption is further

underlined by the results of the free amino acids in the effluents which increases up to 290°C with increasing residence time but drastically drops at 350°C. The same behaviour could be observed in case of phenylalanin save that phenylalanin appears to be less stable than alanin and shows a noticeable degradation at 290°C.

It can be inferred from the results that hydrolysis of peptide bonds occurs at the operating conditions and the residence times employed in the conversion of the ESA-substrate and the indigestible residues from Gent. From this view, the protein content of micro-organisms present in the substrate definitely is not only altered with regard to the secondary and tertiary structure, but also with respect to the destruction of the primary structure, namely the amino acid sequence. This should be evidence that the effluents of the hydrothermal treatment can be considered as being sterile, thus ensuring an additional hygienic barrier in the system.

While the degradation of proteins proceeds with increasing temperature and residence time due to the hydrolysis of the peptide bonds, experiment IV shows that there still is a residual amount of amino acids bound in peptides at conditions which resemble those of the biomass degradation experiments. Therefore it may well be that soluble protein fragments have a contribution to the nitrogen detected in the liquid phase, though probably a very minor one. In order to quantify this contribution, titration of the effluents according to the Kjeldahl-method is envisaged for future experiments.

4.4 Sterility of the effluents

In addition to protein degradation experiments, the sterility of the effluents could be proven by applying standard sterility tests, which are based on the growth of micro-organisms and their detection on different nutrient agars. Figure 8 shows such a sterility test.

Figure 8: Standard sterility test (Merck) for the detection of micro-organisms in aqueous media

By rinsing the effluents over the agar plates and subsequent incubation, colonies become visible in case the effluents were contaminated by micro-organisms. Two different tests were employed, one for the detection of yeasts and moulds (Envirocheck®Contact YM (R) and one for the total viable counts (Envirocheck®Contact TVC). Neither one did show any signs of colonies after incubation, which is further evidence that the high temperature treatment imposes an additional hygienic barrier on the system and ensures biosafety.

4.5 Energy consumption of the mechanical pre -treatment

The energy consumption of the mechanical pre-treatment is difficult to estimate since the solid material received from Partner 1 is very inhomogeneous. In addition, the energy requirement also depends on factors like type and size of the mill, the mode of operation and the water content of the grinding stock. In principle, there are several empirical approaches which may be used to describe the specific energy requirement. One of these approaches is the Bond-equation, which was developed for milling medium sized particles in ball mills:

$$W_m = W_i \left[\left(\frac{x^*}{x_{80,P}} \right)^{1/2} - \left(\frac{x^*}{x_{80,A}} \right)^{1/2} \right]$$

where W_m is the specific energy requirement, W_i is an experimentally determined parameter, x* is the particle size reference value (100µm), and $x_{80,A}$ and $x_{80,P}$ are the 80% undersize of grinding stock and product, respectively.

For the current pre-treatment method, the size reduction is mainly done by a cutting mill. Nevertheless, the bond equation was used to get a first approximate value of the specific energy requirement. For this purpose, the power uptake during operation was calculated by measuring the electric current. The particle size distributions of Gent residues and products were determined by sieve tray analysis. The respective distributions are shown in Figure 9.

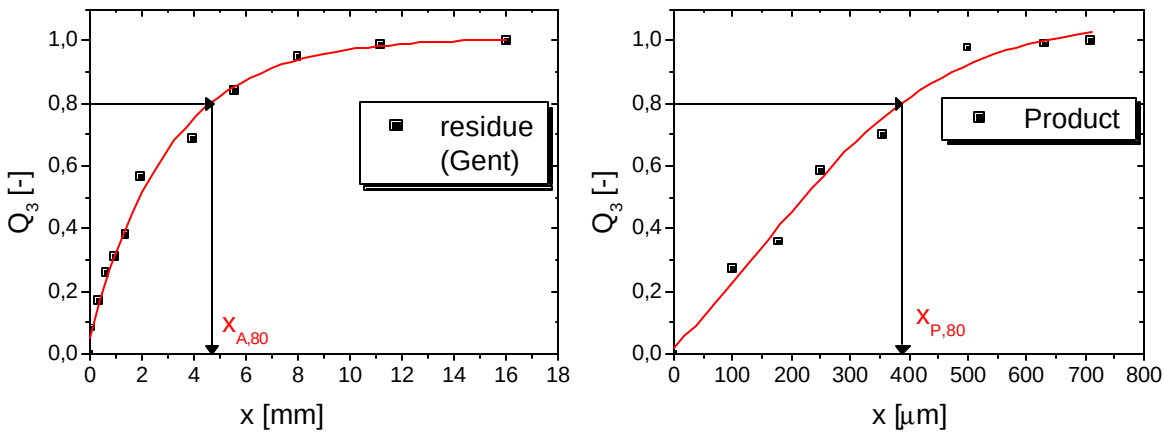

Figure 9: Particle size distribution of Gent residues (left) and ground stock (right)

Reading the corresponding 80% undersize of residue and product, the Bond index can be calculated in case the specific energy requirement W_m is known. W_m is calculated from the electrical power uptake and the measurement of the mass flux through the mill. This calculation gives a specific energy requirement of about 120 J/g, which yields a Bond index of $W_i \approx 90$ kWh/t. As compared to other materials, for which the Bond index typically is less than 20 kWh/t [3], the calculated index seems unreasonably high. On the one hand, this may be due to experimental inaccuracies, which could be a result of the relatively low amounts of solids and the consequently very short milling times, such that the cutting mill was not operating at stationary conditions during the experiment. On the other hand, the Bond equation was derived, as mentioned above, for ball mills. This may have led to significant systematic errors because the empirical Bond equation is not suitable for applying to cutting mills.

Therefore it is recommended to systematically measure the power uptake and the particle size distributions in order to design a proper equation describing and predicting the specific energy requirement for a given size reduction. From this point of view, the calculated Bond index does not seem to be very accurate but it still is meaningful in that it may serve as a rough estimate for the energy requirement.

5 Summary

As agreed on at the 2nd Progress Meeting in Barcelona, first closed loop experiments have been performed by exchanging effluents between Partner 1 and Partner 4. The treatment of solid residues from the methanogenic unit of Partner 1 by the near-critical water treatment yields degrees of liquefaction of about 60 % on a carbon balance within residence times of less than one minute. A considerable increase in liquefaction to more than 80 % could be obtained by acidifying the influent suspension with carbon dioxide.

The degree of liquefaction based on the nitrogen balance is higher than the respective degree calculated for carbon, which is probably due to the fact, that the nitrogen content of the ligno-cellulotic material is comparatively low and the compounds bearing nitrogen are more easily degraded.

In parallel to the liquefaction of residues from Partner 1, the conversion of pure cellulose and bovine serum albumine was studied. For the cellulose experiments, the degree of liquefaction and the formation of sugars were determined at different temperatures and residence times. The experiments using serum albumine show the hydrolysis of polypeptides and the accompanying formation of free amino acids.

It could be proven that the near-critical water treatment ensures an additional hygienic barrier, since it was shown that the reactor effluents were sterile. A convenient mechanical pre-treatment method by means of a newly acquired cutting-mill could be established.

Future perspectives

As discussed at the 3rd Progress Meeting in Hamburg, July 4th 2002, the combination of the methanogenic reactor of Partner 1 with the cellulose degrading treatment step of Partner 2 and the subcritical degradation unit seems to be most feasible and promising from the current point of view. Therefore it is intended to perform further closed loop experiments by exchanging reactor effluents between these partners. In this context, the treatment of effluents from Partner 1 will be continued and the degradation of effluents from Partner 2 will be started as soon as material becomes available. Besides, additional means to enhance the destruction of recalcitrant solid residues will be tested. The potential of acidifying the influents by carbon dioxide has been shown in a preliminary experiment and will be further elucidated. In case there is sufficient time left in the last stage of the project, the addition of oxygen by means of a built-in electrolysis cell will be tested.

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