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Technical Note 86.4.2

on the MAP-Project

"A Total Converting and Biosafe Liquefaction Compartment for MELISSA"

Work Package 4.200: 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 second stage of the project, this paper covers the description of the experimental approach, including the presentation of the flow through type reactor, 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 the latest result of the hydrothermal treatment at subcritical water conditions. In this context, the material balances, a preliminary estimation of the energy requirements, and the results of the fermentation of the effluents are given. The technical note concludes with a summary of the tasks completed in accordance with the work package description (WP. Ref. 4.200) 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 first stage of the project (proof of principle). Based on these results, the influence of operating conditions on the liquefaction of the ESA-substrate is to be studied by varying the operating parameters. This parameter study serves the underlying purpose of characterizing the optimum reaction conditions in terms of degree of liquefaction and biodegradability of the effluent components. In addition, it has to be proven that the effluents of the subcritical degradation do not impose any harmful or toxic effects on the microorganisms employed in the biological reactors, such that the thermo-chemical treatment step can be incorporated in a closed system consisting of biological degradation compartments.

Besides the parameter study and the validation of the non-toxicity of the effluents, the carbon and nitrogen mass balances are to be computed in accordance with WP. 4.200. Additionally, as agreed on at the 2nd Progress Meeting in Barcelona, the feasibility of a freezing step using liquid nitrogen in the preparation of the ESA-substrate was to be studied.

3 Materials and Methods

3.1 Experimental apparatus

Figure 1 shows a sketch of the experimental apparatus.

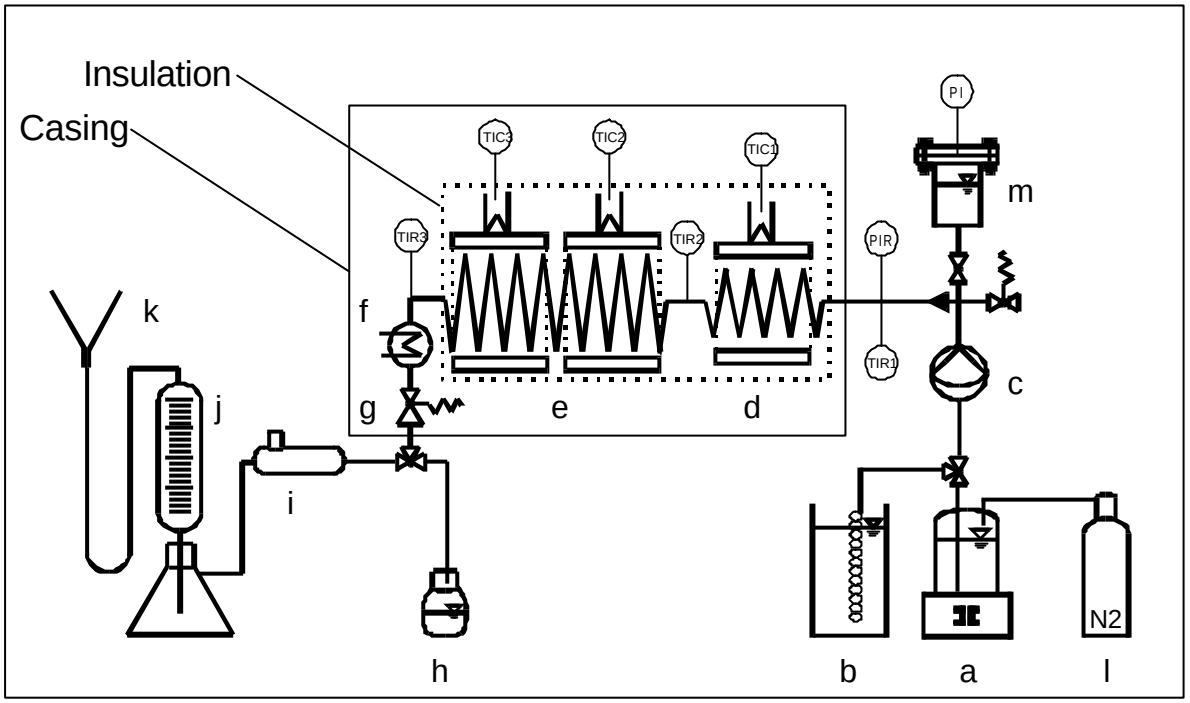


Figure 1: Experimental apparatus: ; *a* feed supply vessel, *b* water storage tank, *c* feed pump, *d* preheater, *e* reactor, *f* effluent cooler; *g* pressure regulator, *h* glass flask, *i* gas mouse, *j* burette, *k* compensator reservoir, *l* compressed gas cylinder, *m* buffer vessel

The core of the tubular reactor consists of a reaction coil made of high pressure piping (V = 50 ml; ID 3.05 mm). The influent suspension is introduced into the system by means of a high pressure membrane pump equipped with double ball valves at the inlet and outlet side. This configuration serves the purpose of ensuring a reliable operation even if one of the ball-seat-units does not function properly as a result of particle deposition between one ball and its respective seat. Leaving the pump the suspension flows through a preheater coil before it enters the reaction unit. Afterwards the effluents are cooled by means of a double pipe heat exchanger operated with tap water as cooling medium. The effluents are subsequently expanded to ambient pressure through a pressure regulator. Liquid effluents are collected in glass flasks, gaseous effluents are collected in a gas trap. The flow rate of the suspension is measured gravimetrically by means of a balance. The volumetric flow rate of the gas phase is determined with a burette system.

The feed vessel containing the influent suspension is agitated by means of a magnetic stirrer to ensure a homogeneous solids distribution throughout the influent. It is operated under a

nitrogen atmosphere by connecting it to a compressed nitrogen cylinder, which prevents oxygen from re-dissolving in the degasified water. The buffer vessel shown in the figure is filled with a nitrogen headspace and serves the purpose of minimizing pressure fluctuations due to the operation of the pump and the expansion valve.

The energy required for heating up the suspension to reaction conditions is introduced into the system by heating jackets, which can be controlled separately. The high temperature part of the setup is insulated to minimize heat losses to the surroundings and it is cased for safety reasons.

The current setup allows operation up to flow rates of 5-6 kg/h, covering temperatures up to 400°C and pressures up to 250 bar.

3.2 Substrate composition

The substrate ingredients, their respective dry matter contents, and the sources they were obtained from are stated in Table 1.

Component	[wt %]	***Source***	DM content [wt %]
Wheat straw	23.3	Local farmer	94.5
Cabbage	23.3	Market	9.7
Soya	23.3	Oil-mill	91.1
Algae	10	BlueBioTechGmbH	95.5
Fecal material	20	In-house production	27.4

Table 1: Substrate composition

All substrate components were used as received and subjected to the size reduction methods described in the following section. The dry matter content of the fecal material was not determined experimentally but calculated from literature data [1].

3.3 Substrate preparation

3.3.1 Current grinding technology

The current preparation of the ESA-substrate consists of a multi-step size reduction procedure in order to obtain sufficiently fine particles that can be handled in the experimental apparatus. This point constitutes a crucial factor in the experimental approach since an improperly

pretreated substrate containing large, fibrous solids bears the risk of a failure of the high pressure pump due to clogging of inlet and outlet valves. Depending on the nature of the substrate ingredients different operations are employed, which are schematically depicted in Figure 2.

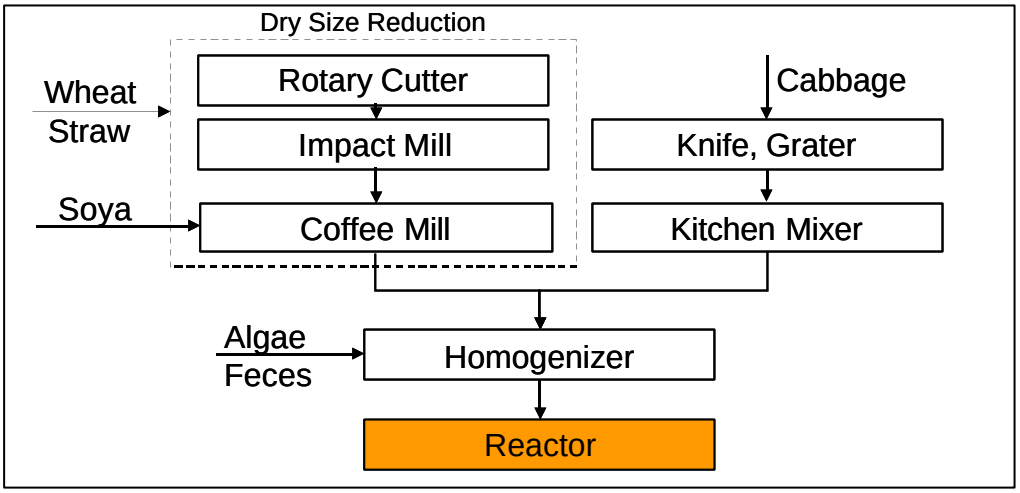


Figure 2: Schematic overview of substrate preparation steps

The cabbage is first treated with a knife and a grater. The resulting pulp is subsequently subjected to a kitchen mixer with the addition of extra water. The algae and the fecal material do not require any additional pre-treatment such that these components are directly homogenized together with the cabbage by means of an Ultra-TORAX.

The grinding of the soya and especially the wheat straw has proven to be the most challenging preparation step. This is currently accomplished by several successive dry cutting and grinding operations. The straw is first fed to a rotary cutter which yields particles in the millimetre range. These fragments are subsequently grinded in an impact mill, where the particles are accelerated in a centrifugal gravity field, hit the blocks of a rapidly rotating disk and disintegrate due to the impact. Afterwards the resulting ground stock is further treated in a conventional coffee mill together with the soya. Finally these components are treated with the Ultra-TORAX in the aqueous phase.

3.3.2 Alternative treatment with liquid nitrogen

As agreed on at the 2nd Progress Meeting in Barcelona, the Department for Thermal Separation Processes was charged with studying the feasibility of freezing the solid samples by means of liquid nitrogen to simplify the cutting and grinding procedure. In order to

investigate the potential of such a treatment, the straw, being the most difficult to grind component of the substrate, was submerged in liquid nitrogen in a mortar. Liquid nitrogen was obtained from the liquid nitrogen supply vessel of TUHH and stored in a DEWAR. The filling of the mortar with liquid nitrogen was achieved by immersing the mortar, held by a crucible tong, in the DEWAR. Figure 3 illustrates this experimental approach.

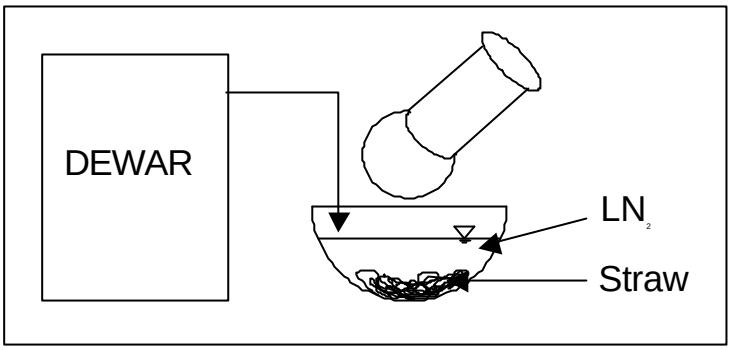


Figure 3: Grinding of the straw in liquid nitrogen

Applying the setup described above, it was intended to grind the straw by means of a pestle. However, the crushing and punching movements of the pestle did not result in a noticeable size reduction of the material, such that the forces introduced by the pestle do not suffice to grind the straw.
The straw was therefore taken out of the liquid nitrogen and immediately filled in a conventional coffee mill. This treatment method also failed to achieve a satisfactory size reduction of the straw, which is probably due to the rapid evaporation of the liquid nitrogen. A direct charging of the mill with liquid nitrogen is impossible, since the extremely cold nitrogen will damage or destroy the mill because of its improper design and construction with regard to such an application.

Different commercial suppliers of grinding and milling equipment were requested about mills cooled by nitrogen for use in lab scale applications. The responses to this inquiry reveal that such a product is not offered by these suppliers.

Summing up these aspects, the use of liquid nitrogen does not seem to be a feasible option in the preparation of the solid matter with the equipment on hand.

3.4 Effluent analysis

3.4.1 Liquid effluents

Influents and effluents are characterized with respect to sum parameters as well as the identification of the main degradation products. The determination of the chemical oxygen

demand (COD) and the amount of ammonia nitrogen (NH_4-N) is accomplished by using standardized cuvette tests (Dr. Lange). Values for total carbon (TC) and total nitrogen (TN) are obtained by means of a TOC analyser (Elementar "HighTOC + TN_b"). In addition, the substrate ingredients were separately burned in a CNS-analyser (model Leco-2000-CNS-Analyser) at an operating temperature of 1100°C in order to measure the molecular composition of these components in terms of carbon, nitrogen, and sulfur content.
The main degradation products are analysed by different chromatographic approaches. Sugar analyses are conducted by means of HPLC with a ligand exchange chromatography (LEC) column. The technical specifications and the operating conditions of this system are stated in Table 2.

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 HPLC system used for the analysis of saccharides

Peak identification and quantification of the components detected with this system are accomplished by injecting standard solutions with known composition at different concentrations, in this way allowing to convert peak areas to concentration values.

Besides the sugar analysis described above, the effluents are analysed with respect to carboxylic acids. Formic acid is detected and quantitatively determined through ion exchange chromatography, acetic acid and higher acids are analysed by means of headspace gas chromatography. In addition to these analyses, the effluents were checked for aldehydes, ketones, and alcohols by headspace GC and direct injection in a gas chromatograph.

3.4.2 Gas phase analysis

Gas samples are taken from the gas trap with a gas tight syringe and are injected in the gas chromatograph specified in Table 3.

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: GC system used for measurement of gas phase composition

The peak areas obtained from the chromatographic analysis are identified and converted to concentration values by injecting gas samples of known composition.

4 Results and discussion

4.1 Molecular composition of substrate components

The molecular composition of the different substrate components was determined in terms of carbon, nitrogen, and sulfur by means of a CNS analyser. The analytical results are reported in Table 4.

Component	C [%]	***S [%]***	N [%]
Wheat straw	39	0.1	0.9
Cabbage	37	0.8	3.7
Soya	39	0.1	1.6
Algae	42	0.7	10.2

Table 4: Molecular composition given on a dry matter basis

Instead of determining the composition of the fecal material experimentally, the values for the nitrogen content were taken from literature [2]. The data stated in Table 4 were applied in all calculations concerning the carbon and nitrogen content.

4.2 Liquefaction of ESA-substrate

4.2.1 Degree of liquefaction based on the carbon balance

The results of the liquefaction experiments in terms of the carbon balance are summarized in Table 5.

No	T [°C]	P [bar]	τ [s]	C_{in} [mg/l]	$C_{out,l}$ [mg/l]	$C_{out,sol}$ [mg/l]	$C_{out,sol}/C_{out,l}$ [%]	$C_{out,g}/C_{in}$ [%]	$(C_{out,l}+C_{out,g})/C_{in}$ [%]	$COD_{out,sol}/COD_{out,l}$	pH [-]
1	300	240	23	3918	3925	2184	55.64	n.d.	100	52.2	4.43
2	307	235	23.6	3925	3507	2552	72.77	0.8	n.d.	55.0	4.01
3	344	240	25.9	3800	3724	2652	71.21	2.5	101	68.3	4.28
4	350	242	28.7	3722	3674	2945	80.16	2.1	101	73.7	4.06
5	352	240	28.4	3761	3746	3089	82.46	2.0	102	72.1	4.04
6	360	245	27.9	3918	-	3321	87.11	2.7	n.d.	74.1	4.20
7	340	238	50.9	-	3603	3419	94.89	n.d.	n.d.	80.7	4.04
8	340	235	25.9	n.d.	3762	2824	75.10	2.6	n.d.	71.3	3.95

Table 5: Carbon balance

All experiments were conducted at initial solid concentrations of about 1 weight percent on a dry matter basis, since higher solid concentrations complicate the pumping of the suspension. Except for the last run, the fecal material was omitted and the other substrate ingredients were adjusted according to their ratios as specified at the 1st Progress Meeting. The effluent of run 1 was reintroduced into the reactor (run 2), thus extending the residence time. The same approach was applied to the effluent of run 6, which was used as a new feed for run 7.

The experimental temperature, pressure, and the residence time calculated on the basis of the reactor exit temperature are stated. The values reported in column 5 are calculated influent carbon concentrations using the molecular composition analysis. Columns 6 and 7 report the measured total carbon concentration in the liquid effluent and the respective values of the dissolved carbon content. The ratio of these concentrations serves as a measure to evaluate the degree of liquefaction based on the carbon balance.

Since the experiments were conducted in a relatively narrow pressure range, the influence of the experimental temperature and the mean residence time on the conversion to soluble carbon components can be studied. A comparison of the first two runs yields an increase of the degree of liquefaction from 56 % to 73 % by increasing the residence time from 23 s to 46 s at a reaction temperature of 300°C. The degree of liquefaction shows an increase with

increasing experimental temperature at comparable residence times, as can be inferred from the results of run 3-6, giving a degree of liquefaction of about 87 % at a temperature of 360°C and a residence time of 28 s. Even higher conversions can be achieved by further extending the reaction time. This can be concluded from the results of run 7, which yields a degree of liquefaction of about 95 % by treating the effluents of run 6 for another 51 s at a temperature of 340°C.

The last experiment was done in the presence of fecal material. Compared to run 3, which was conducted at nearly identical conditions, the degree of liquefaction is slightly higher than in case of the absence of fecal material, which points to the fact that fecal material is more readily decomposed.

The values stated in column 9 report the amount of carbon detected in the gas phase with respect to the calculated influent carbon. As can be inferred from the results of these measurements, the amount of carbon in the gas phase only has a minor contribution, being in the range of 2-3 % of the total carbon introduced into the system.

A comparison of the total effluent carbon, expressed as the sum of the total carbon of the liquid effluent and the gas phase carbon, with the calculated influent carbon is given in the table. The results of this calculation reveal a very good agreement of calculated influent and measured effluent carbon, such that the experimental determinations are very reliable with respect to their accuracy.

The ratio of the chemical oxygen demand of the soluble effluent to the total effluent is reported in the last but one column. Comparing these results with the respective carbon ratios, it can be concluded that the ratio of the oxygen demand is lower than the carbon ratio for all experiments. This can possibly be explained by the presence of highly oxidated compounds, which are soluble in the aqueous phase.

Comparison with cellulose studies:

Figure 4 shows a comparison of the degree of liquefaction with the values obtained from cellulose model studies, which were conducted parallel to the treatment of the ESA-substrate.

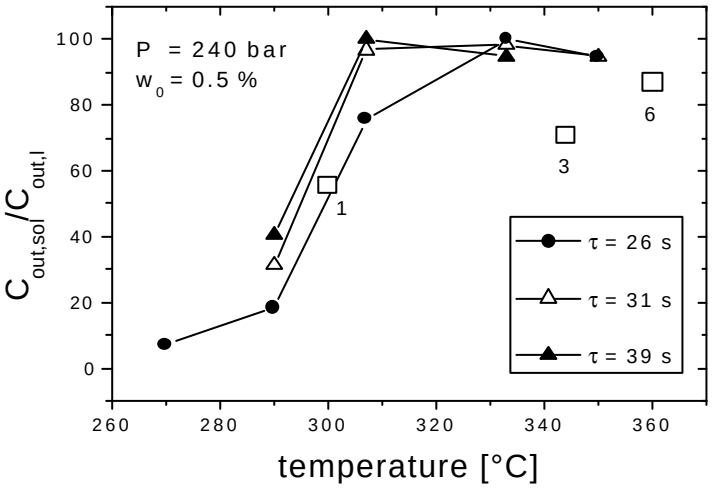


Figure 4: Comparison with cellulose studies, the numbers marking the data points refer to the respective run number of the ESA-substrate experiments

The cellulose suspensions had an initial concentration of 0.5 weight percent and were treated at an experimental pressure of 240 bar. The results show a rapid increase in liquefied carbon in the temperature range between 290°C and 310°C. It can be concluded that at temperatures exceeding 330°C the solid matter conversion in terms of carbon is close to complete for all residence times stated in the figure. The slight decrease in liquefied carbon at higher temperatures and residence times is due to gas formation.
In contrast to these experimental findings, the results of the treatment of the ESA-substrate show a less rapid liquefaction of carbon. While the degree of liquefaction of run 1 is within the range of the cellulose studies, the other runs exhibit a higher insoluble carbon content compared to the cellulose decomposition. This behaviour can be attributed to the presence of components, which are more difficult to degrade, namely lignin, which is cross-linked to cellulose.

4.2.2 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 concentrations were determined using Dr. Lange $N\text{-}NH_4$ cuvette tests. The results of these analyses are summarized in Table 6.

No	$N_{feed,calc}$ [mg/l]	N_{feed} [mg/l]	$N_{feed,sol}$ [mg/l]	N_{out} [mg/l]	$N_{out,sol}$ [mg/l]	$N\text{-}NH_{4,out}$ [mg/l]	$N\text{-}NH_{4,out,sol}$ [mg/l]	N_{out}/N_{feed}	$N_{out,sol}/N_{feed,calc}$	$(N\text{-}NH_4/N)_{outl,sol}$
1	307	405	82	426	283	42.5	40.3	1.05	0.87	0.14
2	n.d.	n.d.	n.d.	457	313	48.0	46.5	n.d.	n.d.	0.15
3	298	405	82	437	323	61.1	59.5	1.08	1.03	0.18
4	292	344	129	392	268	53.6	52	1.14	0.87	0.19
5	***295***	***362***	79	401	289	***57.4***	56.9	1.11	0.93	0.20
6	307	n.d.	130	n.d.	341	86.1	84.0	n.d.	1.06	0.25
7	n.d.	n.d.	n.d.	n.d.	323	81.6	82.5	n.d.	n.d.	0.26
8	376	n.d.	n.d.	475	401	76.5	72.0	n.d.	1.02	0.18

Table 6: Computation of nitrogen balance

The notation of the experimental runs corresponds to the measurements described in section 4.2.1. The calculation of the influent nitrogen concentrations is based on the analysis of the molecular composition of the substrate components. The values of the measured total and soluble nitrogen concentrations of feed and effluent and the respective ammonia nitrogen concentrations of the effluent are reported.

A comparison of the calculated influent nitrogen concentrations with the measured values reveals a discrepancy of 15-25 %. This is partly due to the fact that the dissolved nitrogen was not considered in this calculation. For low partial pressures the solubility of gases in water can be expressed by a linear relationship, which is known as Henry's law:

$$x_{N_2} = p_{N_2} \cdot H_{N_2,l}$$

where x is the fraction of the gas in water, p is the partial pressure of the gaseous component and H is the Henry coefficient. For the system N_2-H_2O at atmospheric pressure and a temperature of 298 K, the Henry coefficient is 0.00065 mol_{N2}/(kg bar) [2], yielding a concentration of about 15 mg N_2 per litre of water. When this portion is taken into account by adding the amount of dissolved nitrogen, the deviation decreases to values of 11-23 %. This discrepancy is probably due to inaccuracies in the determination of the total nitrogen content of the influent.

The nitrogen balance expressed in terms of total effluent to influent nitrogen shows a slight mismatch, which is in the range of 5-15 %. Since the total nitrogen concentration does not decrease but increase, this deviation can only be explained by analytical inaccuracies. Because of the fact that the measured values for total nitrogen seem less reliable than the calculated ones, the degree of liquefaction with respect to nitrogen is computed based on the theoretical values derived from the molecular composition analysis. These values are reported as the ratio of the soluble nitrogen to the calculated total influent nitrogen. With the values of the soluble nitrogen corrected for the gaseous nitrogen dissolved in the liquid phase, it can be concluded that those compounds of the feed which contain nitrogen are readily liquefied. This can be inferred from the fact, that the degree of liquefaction based on the nitrogen balance is higher than the respective values calculated from the carbon balance for all experiments. One possible explanation for this observation may be that the most difficult to degrade substances like ligno-cellulotic materials in general contain little nitrogen.

The measurement of ammonia nitrogen shows that nitrogen in the ammonia form amounts to about 15-25 % of the total nitrogen present in the liquid phase. This result shows that there is a significant amount of nitrogen compounds other than ammonium in the liquid phase which have not been analysed in the experiments so far. Therefore, it is intended to employ additional photometric standard tests for the determination of nitrogen in the nitrate and nitrite form in future experiments, thus improving the nitrogen balance with respect to the unidentified nitrogen species.

4.2.3 Determination of decomposition products

Liquid effluent analysis:

Liquid effluents were analysed for sugars and carboxylic acids. Apart from glucose, which is present in some of the samples in very small amounts, saccharides were either not detected or they were below the limit of quantification of 50 mg/l. These findings are in line with cellulose decomposition experiments, which were conducted parallel to the liquefaction of the ESA-substrate. These model compound studies have shown that at temperatures about 350°C and the residence times applied in the experiments the total saccharide concentration is very low. The two chromatograms below show the sugar concentrations at an experimental temperature of 310°C and a residence time of 24 s (top) and a temperature of 350°C and 26 s (bottom).

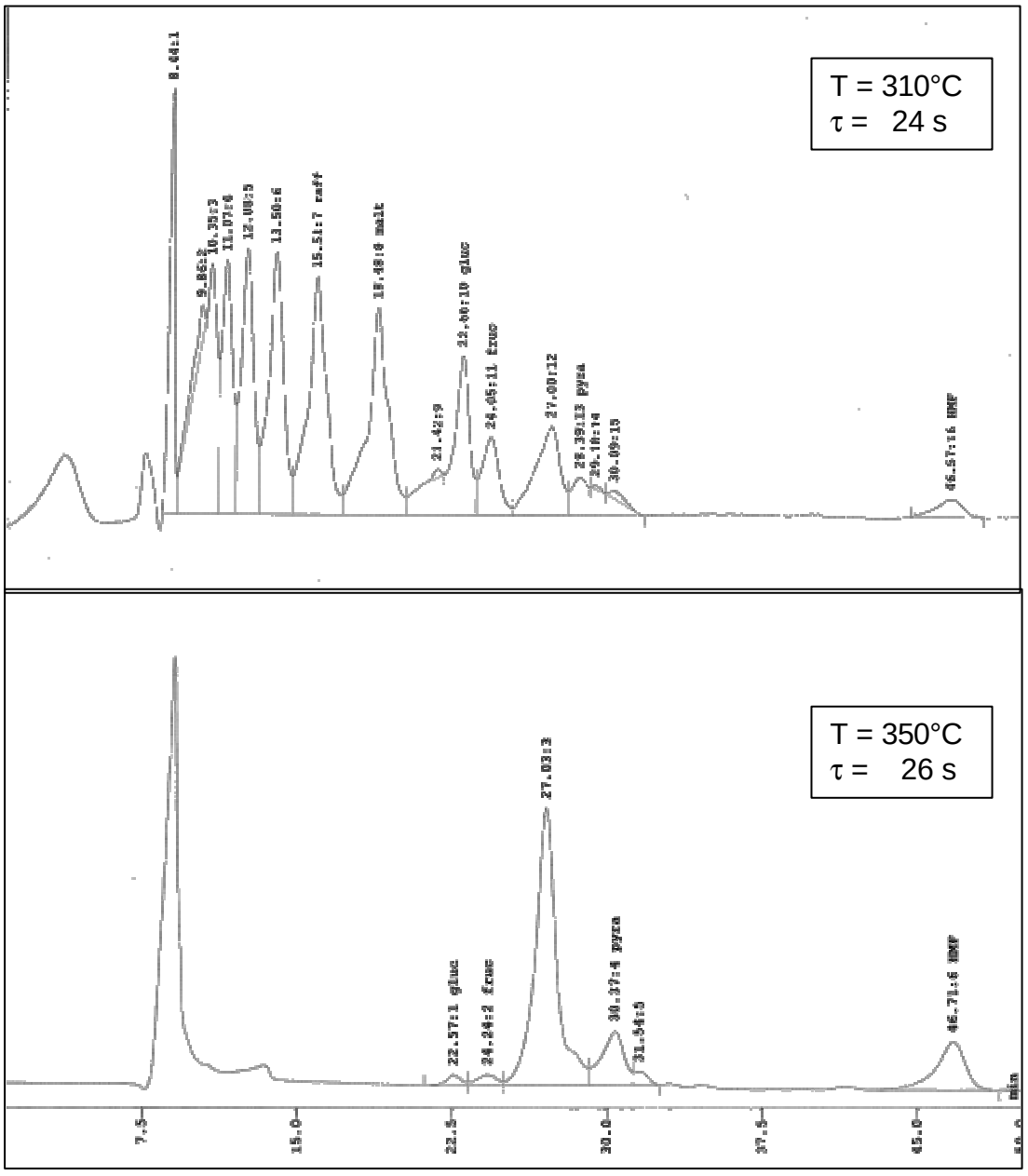


Figure 5: Chromatograms of cellulose degradation experiments

The six components present in the standard, namely raffinose, maltose, fructose, glucose, pyranose, and hydroxymethylfurfural, could be detected in the upper chromatogram. In addition, the chromatogram exhibits distinct peaks at residence times shorter than that of raffinose, which are due to the formation of oligo-saccharides as primary hydrolysis products. In addition to these oligo-saccharides, raffinose, maltose, glucose, and fructose, also small amounts of pyranose and hydroxymethylfurfural could be detected, which are known as secondary reaction products following the cellulose hydrolysis.

In contrast, the chromatogram of the experiment conducted at 350°C shows no more oligo- and mono-saccharides but distinct peaks for pyranose and hydroxymethylfurfural. The major peak at an elution time of 27 s was present in significant amounts in almost all the experiments conducted so far, but was not identified yet. The identification of this degradation product is currently in process.

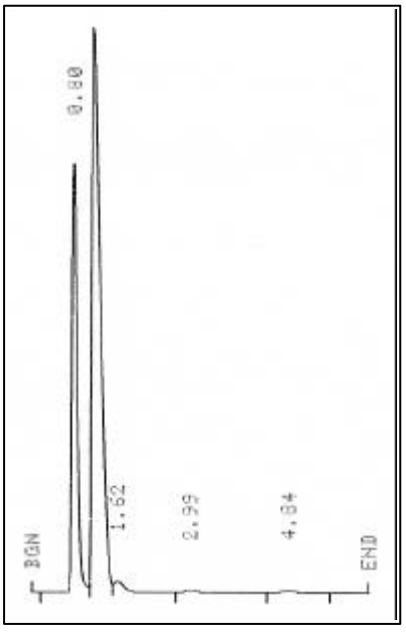
The carboxylic acid analyses for the ESA-substrate experiments shows the presence of formic and acetic acid, which account for up to 20 % of the total soluble carbon. The concentrations of higher acids are negligible.

In addition, effluents of cellulose decomposition experiments were tested for C_1-C_5 alcohols and C_2-C_5 aldehydes by means of headspace chromatography, but were not found in the liquid effluent.

Summing up these aspects, the sugar and acid analysis are established, but the tests for other compounds did not yield positive results so far.

Gas phase analysis:

The figure below shows a typical chromatogram ofobtained gaseous products. The measuring time of this run was 5 minutes at the operating conditions specified in Table 3. The chromatogram obtained from this run exhibits two distinct peaks at 0.80 min and 1.17 min. The first of these two main peaks can be attributed to nitrogen, which is introduced into the system by mixing the feed suspension under a nitrogen atmosphere and by operating the buffer vessel with a nitrogen headspace. The formation of additional nitrogen gas in the course of the reaction is very unlikely and can be excluded on the basis of the nitrogen balance.



The component which is responsible for the second peak at 1.17 min could be identified as carbon dioxide, which is generated in the course of the reaction and contributes to the carbon balance with the amounts stated in Table 5. No other components than nitrogen and carbon dioxide could be detected in any of the experimental runs. The recorded peak areas were converted to concentration values by

injecting gas samples of known composition, meaning known nitrogen to carbon dioxide ratios. The absolute peak areas of the standard samples are in very good agreement with the respective peak areas determined for the effluent measurements, such that no potential other components, that may not be detectable with the current system, are present in the gas phase.

4.3 Fermentation of effluents

Experiments conducted by Partner 3 prior to the toxicity tests, using an experimental set-up similar to the one described below, have shown that the methanogenic fermenter is working with ESA substrate. The effluents of the hydrothermal reactor were fed to a methanogenic bioreactor of Partner 3 in order to investigate the biodegradability and to prove the non-toxicity of the effluent components. Two short-term fermentation tests were done, the first one running for a period of 8 days and the second one for more than 2 weeks. In both cases the thermophilic biomass population, originating from a sewage treatment facility, was operated at a temperature of 50°C with sludge withdrawal, turbid water separation, and subsequent sludge recirculation.

Test 1

The first fermentation was conducted in a 2L reactor with an operating volume of about 1.3 L. In total, an effluent volume of 200 ml per day was fed at 4 rates of 50 ml each, yielding a residence time of about 6-7 days in the bioreactor. Figure 6 reports the biogas production in the course of the fermentation, with day 0 being the starting point of feeding the effluents from the thermal degradation. The effluents were taken from degradation experiments without the addition of fecal material. Prior to the fermentation of the effluents the bioreactor was run with effluents from a delicatessen producer (Nadler). This substrate was obtained from the production of salads and had a high mayonnaise content, thus bearing a high protein and fat load.

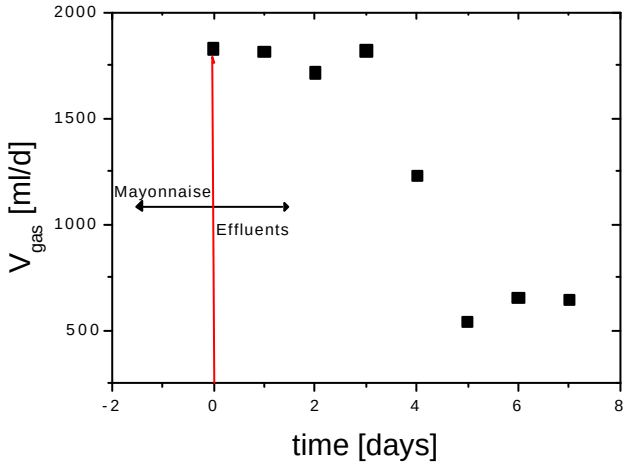


Figure 6: Fermentation test 1: Biogas production

It can be concluded that the change of substrate from the mayonnaise, having a higher carbon load, to the reactor effluents results in a decrease in biogas production after an adaptation period of several days. Afterwards the gas production stabilizes at values of about 600 to 700 ml/d.

Biogas composition and pH values were determined during the fermentation by means of a photometer and a pH probe, respectively.

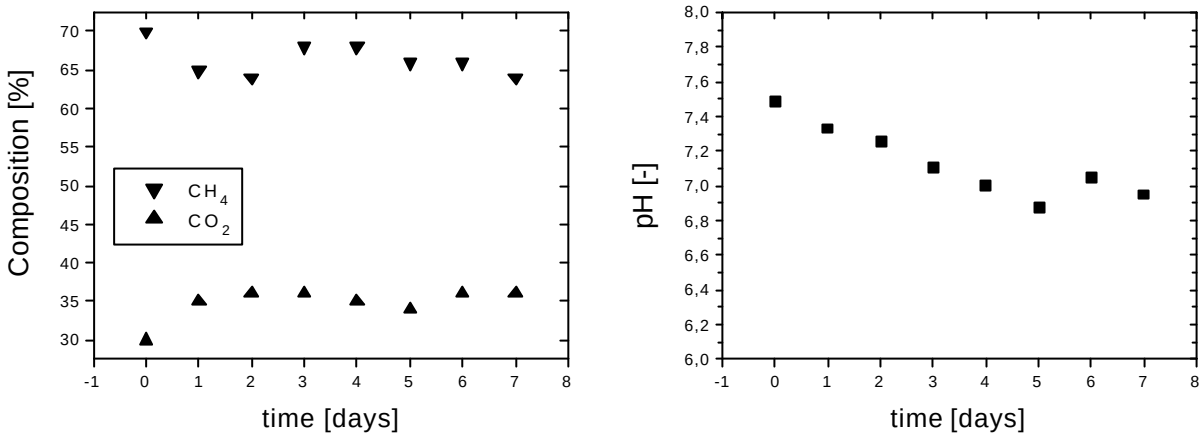


Figure 7: Fermentation test 1:Biogas composition (left) and pH values (right)

The results of these measurements show a stable biogas composition of approximately 65 % methane and 35 % carbon dioxide. The course of the pH over time exhibits a very slight decrease, which may point to an incomplete consumption of acids. The fluctuations of gas production and pH are, however, very minor.

Test 2:

A second fermentation test was conducted using effluents from a thermal degradation experiment which was run with a feed containing all substrate components as specified at the 1st Progress meeting in Gent. The aim of this experiment was to prove a stable operation of the methanogenic bioreactor for more than two weeks and to characterize the effluents in terms of TOC and COD in order to determine the biodegradability of the liquefied material.

The effluents were treated in a 1 L reactor with a feeding of 100 ml of reactor effluents per day. After a period of 10 days, corresponding to one mean residence time, the effluents were collected and analysed in terms of COD and TOC. The specific biogas production with respect to the reactor volume and the course of the pH value during the fermentation are depicted in Figure 8.

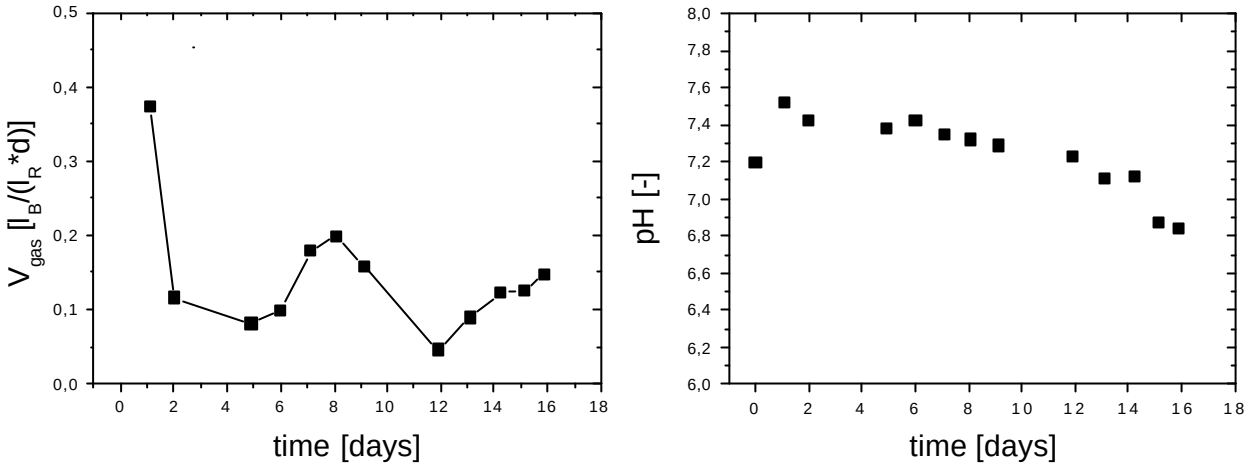


Figure 8: Fermentation test 2: Biogas production versus time (left), pH value (right)

Figure 8 shows that the reactor effluents could be used as sole feed without the addition of any supplementary substrate. The biogas production fluctuates around a mean value of about 0.15 of litres of biogas per litre of reactor volume and day. The pH value shows, again, a slight decrease with increasing fermentation time.

The respective DOC and TOC values for the reactor influent and effluent are reported in the table below. The major part of the influent load is consumed in the methanogenic bioreactor, which can be concluded from the reduction of the respective TOC and COD values. However, this short-term fermentation test cannot reasonably be balanced, since the reactor was filled with sludge, having a higher carbon load, prior to the experiment and only about one reactor volume was exchanged before the first effluent sample was collected.

	TOC [mg/l]	COD [mg/l]
Feed	3717	10760
Effluent (Filtrate)	529	1640

4.4 Energy consumption of the tubular reactor

The energy consumption of the hydrothermal treatment unit can be calculated by applying the laws of thermodynamics and thermochemistry. Since the initial solid concentration of the feed suspension is comparatively low, the energy uptake of the system can be computed by neglecting the enthalpy of reactions and using the properties of pure water for estimating the pumping and thermal energy requirements. The first law of thermodynamics for an open system at stationary conditions is given by following equation:

$$P_{12} + \dot{Q}_{12} = \dot{m} \cdot (\Delta x \cdot g + \frac{\Delta u^2}{2}) + \Delta \dot{H}$$

Assuming that the differences in potential and kinetic energy are neglected this equation can be transformed into an enthalpy balance:

$$w_{12} + q_{12} = h_2 - h_1$$

where w_{12} and q_{12} are the specific work and heat, respectively, which account for the change in specific enthalpy. In order to estimate the energy uptake of the hydrothermal treatment, the above equation is applied to the tubular reactor, assigning water at ambient conditions the state 1 and water at reaction conditions the state 2. By defining this change of state, the theoretical specific energy for pumping and heat requirements can be computed.

The specific enthalpy can be expressed as a function of the operating conditions in terms of temperature, pressure, and density. Expressions for this dependency are taken from [3], which divides the T,P-area into four distinct regions. Region 1 covers the range of liquid water up to a temperature of 623.15K. For this region, the specific enthalpy is expressed by a fundamental equation for the specific Gibbs free energy g(p,T):

$$h = g - T(\frac{\partial g}{\partial T})_p$$

For temperatures exceeding 623.15K (region 3), the thermodynamic properties are calculated on the basis of a fundamental equation for the specific Helmholtz free energy f(ρ,T).

$$h = f - T(\frac{\partial f}{\partial T})_r + \boldsymbol{r}(\frac{\partial f}{\partial \boldsymbol{r}})_T$$

The change of state 1→2, that leads to the enthalpy difference h_2-h_1, can be split by introducing the state 1', which characterizes the conditions at the exit of the high pressure pump. This splitting allows the separate determination of the energy uptake for pumping and the energy introduced into the system for heating the suspension. Figure 9 shows a schematic illustration of the different states and the respective process variables.

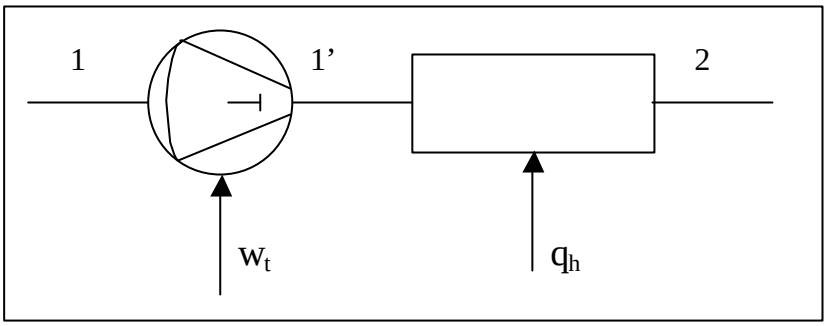


Figure 9: Schematic representation of the energy balance

Assuming that the specific energy for pumping w_t equals $h_{1,1'}$ and that the energy input for heating q_h can be expressed by $h_{1',2}$, the energy requirements for given operating conditions can be calculated.

The following example employing typical operating conditions illustrates this calculation:

State 1: T_1 = 20°C, p_1 = 0.1 MPa; → h_1 = 84.01 kJ/kg

State 1': $T_{1'}$ = 20°C, $p_{1'}$ = 24 MPa; → $h_{1'}$ = 106.26 kJ/kg

State 2: T_2 = 350°C, p_2 = 24 MPa; → h_2 = 1627.56 kJ/kg

The values derived from this calculation show that the specific energy uptake for pumping only has a minor contribution compared to the required heating energy of about 1.5MJ/kg. Heat losses account for the fact that the value of the real heating energy is higher than the theoretically calculated one. However, these heat losses can be minimized by a carefully designed insulation.

An integrated heat design offers the possibility of reutilising part of this energy by means of heat exchangers, which could provide energy for various heating purposes on a lower temperature level.

4.5 Energy consumption of the mechanical pretreatment

The energy consumption of the mechanical pretreatment is difficult to estimate since the current substrate preparation consists of a number of subsequent size reduction steps. 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 future experiments, it is intended to treat dry particles by means of a new lab-scale cutting mill, thereby reducing the required number of preparation steps. For this approach it may be possible to estimate the required energy consumption by measuring the power uptake and the milling time and subjecting the particles to a sieve analysis before and after milling. However, it is questionable if this approach leads to an accurate determination of the adjustable parameter W_i, such that the results from the lab-scale mill can be transferred to different types of mills and scales. However, the measurement of the power uptake may serve as a rough estimate for the energy requirement of the mechanical pretreatment.

5 Conclusions

The results presented in this technical note show the feasibility of the hydrothermal degradation of the ESA-substrate at subcritical water conditions. High degrees of liquefaction could be achieved within short residence times at the temperatures and pressures applied in the experiments. The variation of the operating conditions in terms of temperature and residence time shows an increase of liquefied carbon with increasing temperature and time, leading to a close to complete conversion at about 350°C and a residence time in the range of one minute.

The nitrogen and carbon balances show a good match. 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.

The degrees of liquefaction of the ESA-substrate are lower than the respective values of pure cellulose, which can be explained by the presence of compounds like lignin, which are more difficult to degrade by the hydrothermal treatment.

Two short term fermentation tests were done in order to prove the non-toxicity of the reactor effluents. The results of these tests show that the effluents could be used as substrate for the micro-organisms without any observable detrimental effects. A detailed analysis of the biodegradability in terms of biogas production and COD reduction requires longer fermentation times and cannot be conducted based on these tests.

The incorporation of a freezing step by liquid nitrogen in the substrate preparation was studied but does not seem to be a promising alternative to the current grinding procedure.

Future perspectives

As agreed on at the 2nd Progress Meeting in Barcelona, the next step of the project will be the treatment of the solid biomass material from the methanogenic reactor of Partner 1. In addition, the parameter study with respect to the experimental conditions will be continued as well as the characterization of the liquid effluents.

Literature:

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2 NIST Chemistry WebBook, National Institute of Standards and Technology, http://www.nist.gov

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