MELiSSA

TECHNICAL NOTE

Memorandum of Understanding TOS-
M T/2002/3161/In/ L

TECHNICAL NOTE: 4.6

TESTING OF ADDITIONAL LIQUEFACTION TECHNOLOGIES WITH SUBSTRATE FROM PARTNER 1,2

---

prepared by/*préparé par*	Tobias Albrecht, Gerd Brunner TU Hamburg-Harburg, Thermal Process Engineering
reference/*réference*	14719/00/NL/SH
issue/*édition*	1
revision/*révision*	0
date of issue/*date d'édition*	30/11/04
status/*état*	Draft
Document type/*type dedocument*	Technical Note
Distribution/*distribution*	

CONFIDENTIAL DOCUMENT

APPROVAL

Title *titre*	issue 1 *issue*	revision 0 *revision*

author *auteur*	date *date*

approved by *approuvé by*	date *date*

CHANGE LOG

reason for change /*raison du changement*	issue/*issue*	revision/*revision*	date/*date*

CHANGE RECORD

Issue: 1 Revision: 0

reason for change/*raison du changement*	page(s)/*page(s)*	paragraph(s)/*paragraph(s)*

TABLE OF CONTENTS

1 INTRODUCTION

This Technical Note covers the latest results of the hydrothermal treatment of biomass and model compounds thereof in nearcritical water. In addition to the tasks described in WP 4.6 and WP 4.7 this note includes a report of the additional work assigned to the Department of Thermal Process Engineering at the last Progress Meeting held in Noordwijk on May 12th 2004.

Based on the results of the Technical Note 4.5 it could be concluded that the acidification by carbon dioxide is a proper means to enhance the rate of cellulose decomposition in subcritical water and to increase the yield of monomeric sugars. While in case of pure crystalline cellulose a complete conversion to water-soluble substances could be achieved, the use of carbon dioxide did not prove to be as efficient in treating lignin and ligno-cellulotic materials like wheat straw. For such wastes, the treatment with carbon dioxide and the resulting decrease in pH did not result in complete liquefaction but left a significant portion of insoluble substances based on a carbon balance. This residual, very recalcitrant fraction can probably be attributed to lignin. Because of this conclusion preliminary experiments adding hydrogen peroxide as an oxidant were conducted. In these experiments the SCWO-technology (Supercritical Water Oxidation) was applied to lignin and wheat straw. The effluents obtained from the oxidative treatment were absolutely solid-free and had a dissolved organic carbon content corresponding to 10-20 % of the total influent carbon. These results indicate that the influent carbon, which mostly consists of water-insoluble compounds, can be completely converted to water-soluble substances and gaseous species in the course of the oxidative destruction.

Having already shown the catalyzing effect of carbon dioxide in liquefying pure cellulose, the focus of the present Work Package was laid on the oxidative treatment employing hydrogen peroxide as the oxidizing reagent. Following the preliminary experiments with lignin and wheat straw, additional runs varying the operating conditions in terms of temperature and stoichiometric excess were conducted. As agreed on in WP 4.6, closed loop experiments with solid residues received from Partner 1 and Partner 2 were performed. The hydrolysates were distributed to Partner 1 and analyzed with respect to the dissolved organic carbon content and the concentration of carboxylic acids.

During the last Progress Meeting, severe concerns were raised whether the hydrothermal treatment might possibly transform organic substances into more harmful reaction products. In the frame of a HACCP analysis, the Department of Thermal Process Engineering was assigned to select a proper model compound in collaboration with Partner 1 and proceed with the experimental studies. The compounds under consideration were polycyclic aromatic hydrocarbons and polychlorinated biphenyls, which were regarded as being insusceptible to biological degradation and thus biologically persistent. Since there are restrictions in handling with respect to the latter class of compounds, it was agreed with Partner 1 to use naphthalene for these studies.

In addition to the experimental studies with naphthalene, a comprehensive literature survey about the hydrothermal conversion of polychlorinated biphenyls was done. This Technical Note also includes a short compilation of some papers published in this field recently. The most important results and conclusions are summarized.

For the characterization of solubles released during the hydrothermal treatment, time was spent on establishing a GC-MS method and conducting test runs.

2 MATERIALS AND METHODS

Experimental set-up:

The model compound studies with naphthalene and lignin and the closed loop experiments with non-degradable biomass from Partner 1 and Partner 2 were conducted in the continuous flow reactor described in detail in the preceding Technical Notes. The influent suspension is introduced into the system by means of a high pressure membrane pump and moderately preheated to avoid the onset of thermo-chemical decomposition before the reaction unit. Pure water is fed to the system by a separate line and heated to high temperatures upstream of the mixing point. By mixing the two streams in a mixing tee the temperature of the influent suspension can instantaneously be raised to the desired level, resulting in a controlled start of the reaction. The biomass is treated at isothermal conditions and cooled down immediately by a double-pipe heat exchanger coupled to the outlet of the tubular reaction unit. Figure 1 shows a schematic sketch of the experimental apparatus.

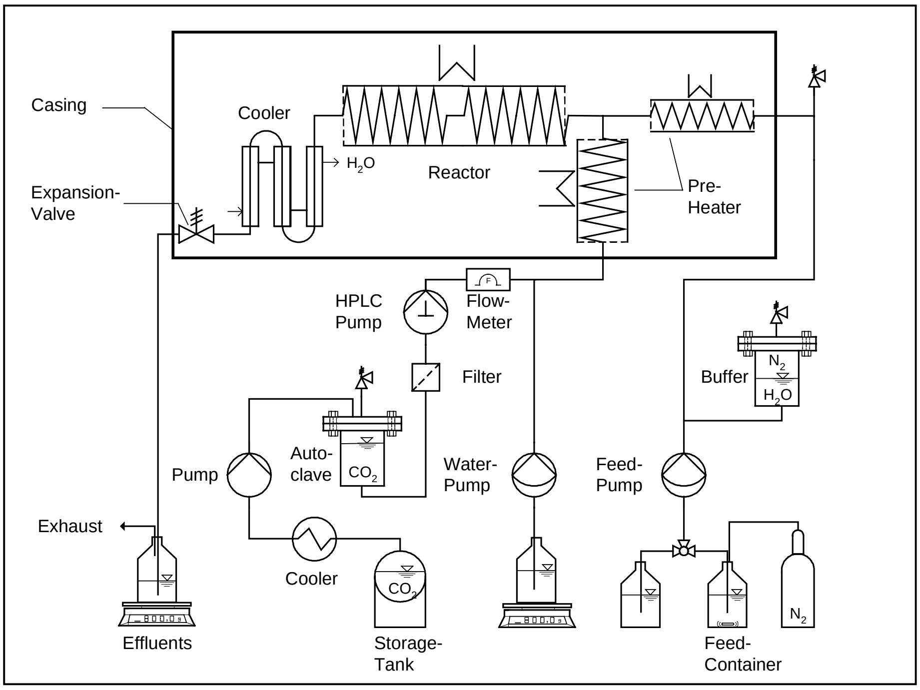

Figure 1: Schematic sketch of the experimental apparatus

The residence time within the reactor can be varied to a certain degree by adjusting the pump settings and by installing tubular reaction units of different length and corresponding internal volume. The third line delivering carbon dioxide to decrease the pH of the influents was not used in the studies presented in this Technical Note.

Materials:

In the frame of the HACCP-analysis studies on the thermal decomposition of polycyclic aromatic hydrocarbons were conducted with naphthalene (Sigma-Aldrich). The naphthalene was used as received. For stabilizing the water-naphthalene suspension an emulsifier, Triton-X, had to be added to the system.

The model compound studies on the hydrothermal degradation of ligno-cellulotic materials were done with pure alkali lignin (Sigma-Aldrich).

The closed-loop experiments on the decomposition of biologically non-degradable solid matter were done with the solid residues received from Partner 1 and Partner 2. The material was stored in a refrigerator prior to treatment. The samples were received as mixed liquor containing the solid residues as well as considerable amounts of liquids. In order to guarantee a reproducible amount of solid material for each experimental run, the samples were dried by evaporating the liquids prior to treatment. The samples were placed on dishes and dried at room temperature under a hood over night.

In the studies on the oxidative treatment of biomass hydrogen peroxide (Sigma-Aldrich) was applied as the oxidizing reagent and was used as received.

Analytical methods:

Several analytical approaches were employed for characterizing the reaction effluents as well as the starting materials. The solid residues received from Partner 1 and Partner 2 were analysed for the carbon, nitrogen, and sulphur content by burning samples in an elementary analyser (Leco-2000-CNS) and measuring the respective gaseous oxidation products in the offgas. The amount of liquefied organic compounds was determined by measuring the dissolved organic carbon content in a DOC analyser (Analytik Jena „multi N/C 3000“) as a lumped parameter to characterize the degree of conversion to water-soluble substances.

Additional gas-chromatographic approaches have been applied to characterize the solubles released during the hydrothermal treatment in more detail. Three different methods have been employed to quantify the concentration of carboxylic acids, which are known to be relatively stable oxidation products, to quantify the residual amount of naphthalene after hydrothermal treatment, and to identify further degradation products. These methods are described in the following.

The reaction effluents were analysed for carboxylic acids with the GC system of Partner 3. This system consists of a gas chromatograph (Varian 3900) equipped with a capillary column (WCOT fused silica) and a flame ionisation detector operated at 220°C. The samples are acidified by 2 % phosphoric acid prior to injection. For each run a sample volume of 0.5 µl was injected using nitrogen as carrier gas. The temperature program is as follows: After an initial holding time of 1 min at 60°C the oven temperature is increased by a rate of 10°C/min to the final temperature of 200°C. By this method carboxylic acids higher than formic acid can be detected and quantified. Formic acid cannot be detected by FID but would require alternative methods like HPLC for detection.

The residual amount of naphthalene was determined by the method described in Table 1.

Technical Specifications	GC	Hewlett Packard 5890
	Column Type	Capillary Column, J & W DB5; L = 30 m, i.d. = 0.25 mm, film thickness = 0.1 µm
	Detector Type	FID
Operating Conditions	Carrier Gas	Nitrogen
	Injected Volume	1 µl
	Solvent	Toluene
	Injector Temperature	300°C
	Detector Temperature	350°C
	Oven Temperature	T_{start}: 100°C (2 min), heating rate: 10°C/min, T_{final}: 320°C (7 min)

Table 1: GC method for analyzing naphthalene, technical specifications and mode of operation

The aqueous effluents were treated by single-stage liquid-liquid extraction with toluene. The residual naphthalene was quantified by preparing external standards of different naphthalene concentration and evaluation of the peak area ratios.

In addition to the quantification of carboxylic acids and the residual naphthalene content a GC-MS method was tested for the characterization of further, unknown degradation products. The GC-MS system consists of a HP 5890 GC coupled to a HP 5989A MS engine by a heated interface. The ionisation is accomplished by EI (70eV). The separation was done with a capillary column (FS-Supreme-5, i.d.: 0.25 mm, df: 0.25 µm, L: 30 m) using helium 5.6 as carrier gas. The temperature program applied is as follows: initial temperature 100°C (2 min); heating rate 10°C/min; final temperature 320°C (7 min). The aqueous effluents were extracted with toluene and dichloromethane and a sample of 0.5 µl was injected in splitless mode.

3 RESULTS AND DISCUSSION

3.1 Conversion of PAHs and PCBs in sub- and supercritical water

Destruction of PCBs:

Based on the work of *Modell et al.* in the 1980s, several research groups have studied the feasibility of destroying PCB-contaminated hazardous wastes in sub- and supercritical water. This research was aimed at the treatment of highly concentrated wastes, e.g. oils from capacitors or electrical transformers, where PCBs have been applied in large quantities in the past. The most important results are summarized below, emphasizing the degree of PCB-conversion and the characterization of decomposition products.

The destruction of PCBs under both oxidative and alkaline conditions was studied by *Weber et al.* [1]. In this investigation a PCB mixture containing mainly DiCB and HeptaCB as well as measurable amounts of MonoCB, OctaCB, NonaCB and DecaCB was used. Of this mixture about 100-1000 µg were loaded along with 11 ml of water into a microautoclave (44ml volume) made of Hastelloy C-276 for the oxidative treatment. For these studies the autoclave was filled with oxygen providing an overstoichiometric amount of oxidant. For the non-oxidative treatment, the autoclave was loaded with 11 ml of sodium hydroxide solution (0.1 molar) and flushed with argon. The results of both destruction processes in terms of the degree of conversion, stated as the destruction efficiency, are given in Figure 2.

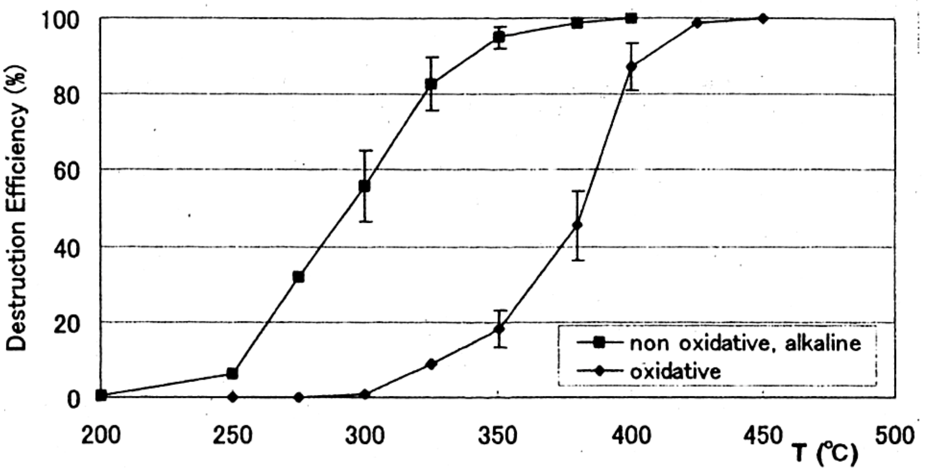

Figure 2: Destruction efficiency of PCB in subcritical and supercritical water under oxidative conditions and alkaline conditions, 15 min, [1]

The results reveal a remarkable thermo-chemical stability of the PCBs used in this study. In case of the oxidative treatment, temperatures in the near-critical region led to a PCB-destruction of about 50 % at a treatment time of 10 min. An essentially complete conversion could be observed at temperatures markedly exceeding 400°C. In contrast, the non-oxidative, alkaline treatment led to higher destruction efficiencies at given operating temperature.

In addition to the destruction efficiency, the authors studied the product formation, which was shown to be dependent on operating temperature and treatment time. The toxicity of the effluents was assessed in terms of toxic equivalency and compared to the influent PCB mixture. During the early stage of the reaction, the formation of polychlorinated dibenzofurans (PCDF) could be observed, while no polychlorinated dibenzodioxins (PCDD) could be detected. The temporary increase in PCDF concentration results in an increase in toxic equivalency of the reaction mixture as compared to the inlet PCB mixture. However, the treatment at prolonged reaction times and elevated temperatures results in the subsequent destruction of PCDFs, since this class of compounds is not stable but constitutes an intermediate product only. This finding is in line with the results from other research groups (*Gräbel and Hagenmaier*, *Yamaguchi et al.*), who could show the ability of supercritical water to destroy PCDFs and PCDDs.

In fact, an increase in reaction time from 15 to 60 min at 400°C led to a drastic decrease in toxic equivalency. At a temperature of 450°C, reaction times exceeding 15 min resulted in PCDF-concentrations below the detection limit. These results prove the ability to convert a biologically persistent class of substances to harmless end products by employing SCWO-technology, provided that the operating conditions are carefully selected when expecting any significant PCB-levels in the influent.

Based on the experimental results the authors propose a reaction mechanism and illustrate possible initial reaction pathways.

The destruction of a single-chlorinated biphenyl, namely 3-chlorobiphenyl, is reported by *Hatakeda et al.*[2]. In this study the PCB was converted in a continuous flow reactor by adding hydrogen peroxide as the oxidant. It is stated that PCB-conversions higher than 99.9 % can be obtained at a temperature of 400°C and residence times exceeding 10 seconds in case an excess of oxidant is provided. The authors present a table of reaction products for an experiment in which half the stoichiometric demand of hydrogen peroxide was used. Again, various PCDFs could be detected in small amounts, but no PCDDs were found in the effluents.

The oxidative conversion of a tetra-chlorinated biphenyl in the presence of methanol was investigated by *Anitescu and Tavlarides* [3]. In this study an isothermal plug-flow reactor with achievable residence times of 3.11 seconds at 500°C and 25.6 seconds at 400°C was employed for the destruction of PCB in the presence of hydrogen peroxide as the oxidant. The authors come to the conclusion that adding methanol to the influents enhances the rate of PCB destruction, possibly by promoting the dechlorination step due to the formation of reactive intermediates originating from the methanol. Regarding the product formation, no PCDFs were detected in the presence of methanol as a co-solvent. Based on the experimentally derived data a rate equation for the destruction of PCBs along with possible reaction pathways is given.

In addition to the oxidative destruction of PCBs, *Sako et al.* [4] also studied the non-oxidative dechlorination of PCBs by means of supercritical water hydrolysis in the presence of sodium hydroxide as an alkali catalyst. The transformation of PCBs was conducted in a batch type reactor with an internal volume of 9 cm^3, which was loaded with 10 mg of PCBs and 1.3 g of water giving a reaction pressure of about 30 MPa at a temperature of 450°C. Two different PCBs were studied with respect to the dechlorination at varying amounts of sodium hydroxide and the decomposition at different hydrogen peroxide concentrations. The reaction time was set at 20 min at a constant temperature of 450°C for all experiments. The results of these studies are depicted in Figure 3.

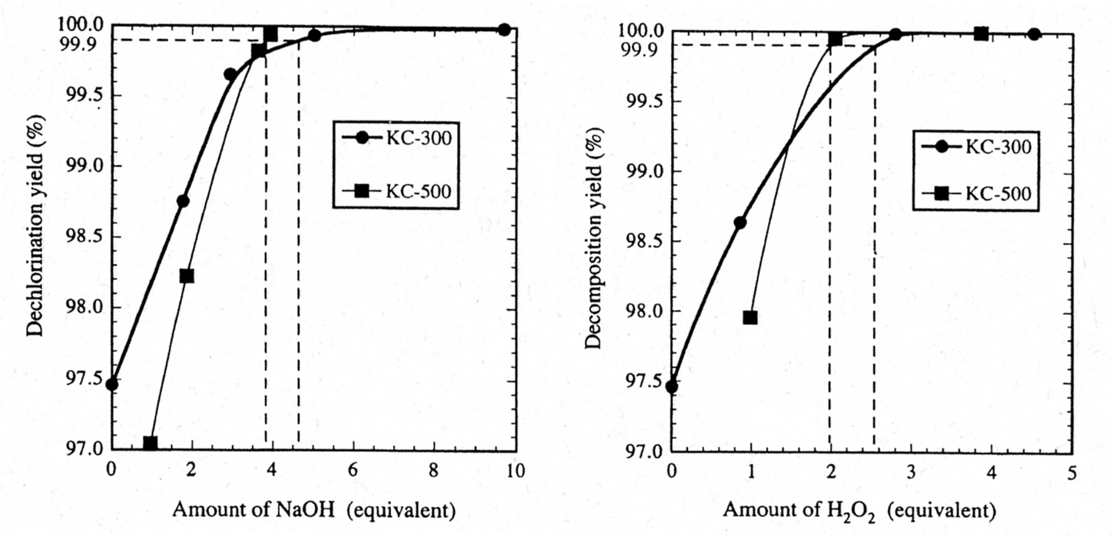

Figure 3: Dechlorination of pure PCBs with SC-water + NaOH, 723 K, 30 MPa, 20 min, PCB/water = 1 wt% (left); Decomposition of pure PCBs with SC-water + H_2O_2, 723 K, 30 MPa, 20 min, PCB/water = 1wt% (right), [4]

It can be inferred that adding sodium hydroxide increases the degree of dechlorination from 97.5 % to values higher than 99.9 %. Major decomposition products of the dechlorination were phenol, biphenyl, and hydroxybiphenyl. Although no oxidizing reagent was charged to the reactor, the total organic carbon content decreased to about half the initial value, which was probably due to the formation of gaseous species.

Regarding the oxidative destruction of biphenyls, an amount of 2-3 times the stoichiometric demand results in an essentially complete decomposition at the conditions applied.

Destruction of PAHs:

As agreed on at the last Progress Meeting experiments were performed on the hydrothermal decomposition of polycyclic aromatic hydrocarbons, since the use of PCBs is prohibited due to governmental restrictions. Naphthalene was employed in the model compound studies since it is classified as being irritating but non-toxic. In addition, it constitutes the simplest compound of all polycyclic aromatic hydrocarbons and is therefore especially suitable for studying the product formation in the course of the hydrothermal transformation.

Experiments were conducted systematically varying the operating temperature and the amount of hydrogen peroxide with respect to the stoichiometric demand. The results of these experimental runs applying an initial naphthalene concentration of 0.5 wt% and a pressure of 25 MPa are shown in Table 2.

Run No	T [°C]	τ [s]	Amount of H_2O_2	$DOC_{out, meas}$ / $TC_{in, calc}$ [%]	C_{acids} / C_{diss} [%]
1	375	65	0	8.8	2.3
2	263	79	0	3.9	5.2
3	384	7	2	1.9	28.3
4	375	11	2	2.9	72.6
5	292	12	2	4.2	54.2
6	380	8	2	5.7	51.8
7	302	10	2	14.8	37.0
8	384	7	0.5	60.5	1.9
9	375	8	0.5	23.9	5.1
10	384	6	0.5	31.9	6.3

Table 2: Naphthalene conversion to soluble products on a carbon basis: P = 25 MPa, the amount of H_2O_2 is given with respect to the stoichiometric demand, initial solid concentration: 0.5 wt%

For run number 1 and 2 an additional reaction unit was coupled to the tubular reactor to prolongate the reaction time. These runs show that naphthalene is relatively stable under non-oxidative conditions. At well-subcritical conditions (263°C) only 4 % of the inlet carbon is converted to water-soluble substances, while in the near-critical region (375°C) about 9 % of the total carbon is liquefied at residence times exceeding 1 minute. The effluents of these experiments exhibit a characteristic naphthalene odour and are similar in appearance to the influent suspension. These observations indicate that naphthalene is only degraded to a minor extent by hydrolytic attack.

In contrast, the oxidative treatment (run 3-10) substantially transforms naphthalene within reaction times of about 10 seconds. The effluents of these experiments were absolutely solid-free, showing that naphthalene was converted completely to water-soluble substances and gaseous species. Supplying twice the stoichiometric demand (run 3-7) results in a degree of liquefaction of less than 6 %, meaning that the remaining carbon was completely mineralized. Especially the experiments conducted at near- and supercritical conditions exhibit a very minor contribution of dissolved carbon, which amounts to less than 3 % of the total influent carbon. Highly oxidized carboxylic acids, mainly acetic acid, account for a significant portion of the dissolved carbon, ranging from about 30 % to more than 70 %.

Applying half the stoichiometric demand of hydrogen peroxide results in a partial oxidation of naphthalene (run 8-10). In these experiments, a considerable portion of the total carbon could be detected as dissolved carbon (24-61 %). The amount of highly oxidized carboxylic acids is less (2-6 %) than in case of the runs with overstoichiometric oxidant supply.

These results were basically confirmed through quantitative measurements of the residual naphthalene content applying the GC method described above. Measurable amounts of naphthalene could only be detected for the non-oxidative experiments (run 1,2) and run 10. In case of run 1, the concentration of naphthalene determined by GC analysis exceeded the influent concentration, which is probably due to incomplete mixing of the suspension during the taking of the sample for the liquid-liquid extraction with toluene. The naphthalene conversion calculated for run 2 is 16 %, which appears to be rather high when compared to the results of the DOC analysis (4 %). This might also be a problem of incomplete mixing in the sample vial, meaning that the amount of naphthalene in the aqueous phase used for liquid-liquid extraction deviates from the naphthalene content in the effluent suspension. Run 10 exhibits a low residual naphthalene content corresponding to a degree of conversion of 99.1 %.

The data depicted in Table 2 reveal a significant portion of dissolved organic carbon, which cannot be attributed to carboxylic acids higher than formic acid. The contribution of formic acid cannot be assessed by GC-FID. Therefore, the GC-MS method described above was employed in the Department of Thermal Process Engineering for the identification of further degradation products. Although considerable effort was spent to optimize the system, the analyses still suffer from a poor sensitivity. This lack of sensitivity is not due to an improper mode of operation but must be ascribed to a technical or maintenance problem with the MS engine itself. So far the cause of insufficient sensitivity has not been clarified, but there are several possible explanations such as problems with the high vacuum system, deteriorated insulators in the ion source or a defective electron multiplier. Since the trouble shooting has not been successful so far, selected samples of the naphthalene experiments were analysed in the Central Analytical Laboratory of the Technische Universität Hamburg-Harburg.
The system used for the analyses was a HP5890 gas chromatograph with a HP5971A MS engine. A two-step temperature program was applied for separating the reaction products on a capillary column (DB-5ms): Starting temperature: 70°C (2 min) with a subsequent heating rate of 5°C/min to 170°C and a following heating rate of 10°C/min to 290°C and a final holding

time of 10-15 min at 290°C. An aqueous sample of 4 ml was extracted with an equivalent volume of dichloromethane.

Three samples (run 1,7, and 10) representing non-oxidative and oxidative conditions at different amounts of oxidant were selected. The chromatogram of run 1 is shown in Figure 4.

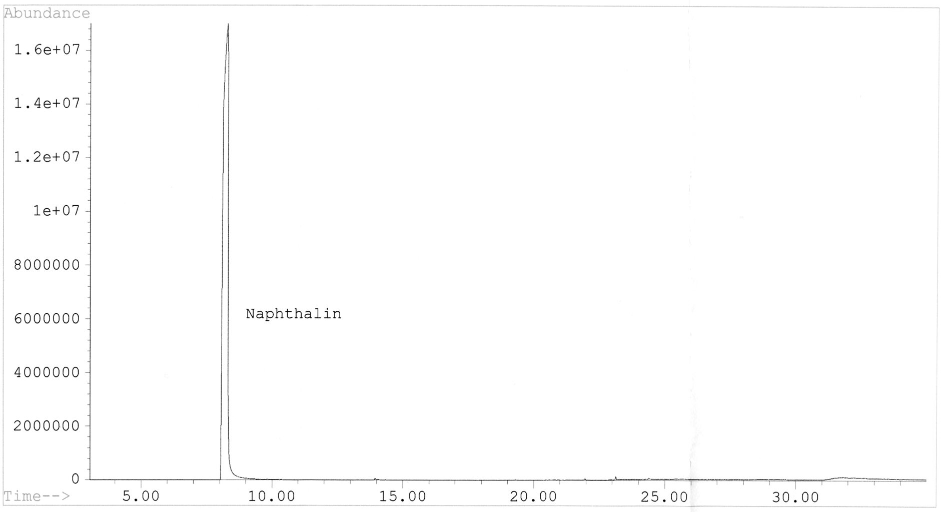

Figure 4: <u>T</u>otal <u>i</u>on <u>c</u>hromatogram (TIC) of run 1 : Non-oxidative treatment at 375°C, 65 s

It can be concluded that no compounds other than naphthalene are present in significant amounts. This observation is in line with the results of the DOC analysis and the quantification of residual naphthalene by GC-FID. The pattern changes substantially for run 10, in which half the stoichiometric demand was applied (Figure 5).

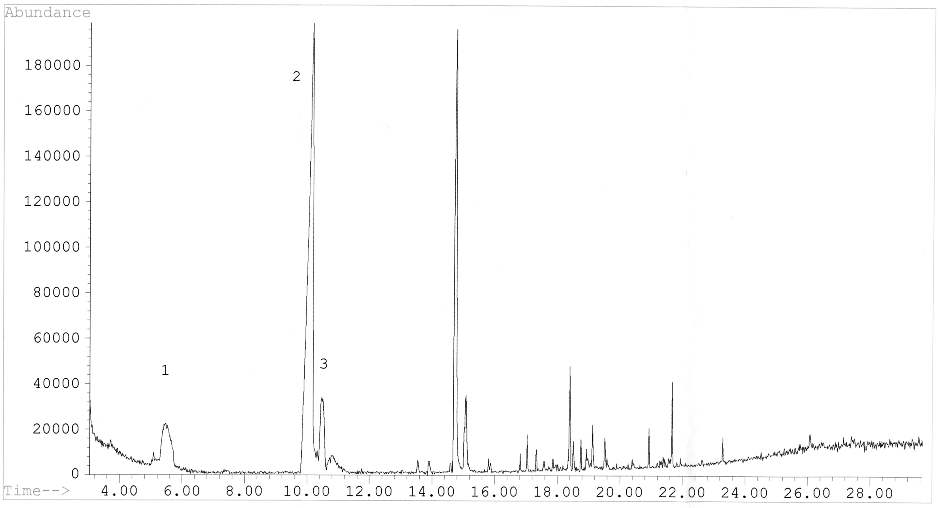

Figure 5: <u>T</u>otal <u>i</u>on <u>c</u>hromatogram (TIC) of run 10 : Partial oxidation treatment at 384°C, 6 s, 1: Phenol, 2: Benzoic acid, 3: Naphthalene

Apart of small amounts of residual naphthalene (3) phenol (1) and benzoic acid (2) could be identified as major degradation products of the partial oxidation. By means of a two-point external calibration phenol, benzoic acid, and residual naphthalene could be analysed quantitatively. Along with the carboxylic acids these compounds amount to about 60 % of the dissolved organic carbon. The residual fraction can be partly attributed to further organic substances extracted by dichloromethane (see below). Formic acid might have a significant contribution, too. In addition, it is very likely that polar, hydrophilic compounds other than carboxylic acids are formed in the course of the partial oxidation. This can be inferred from the detection of additional peaks by the GC method used to quantify carboxylic acids. However, these peaks were not identified.

As compared to the partial oxidation, the oxidative destruction supplying excess oxidant (run 7) yields less degradation products at a lower concentration level. Figure 6 shows the respective chromatogram.

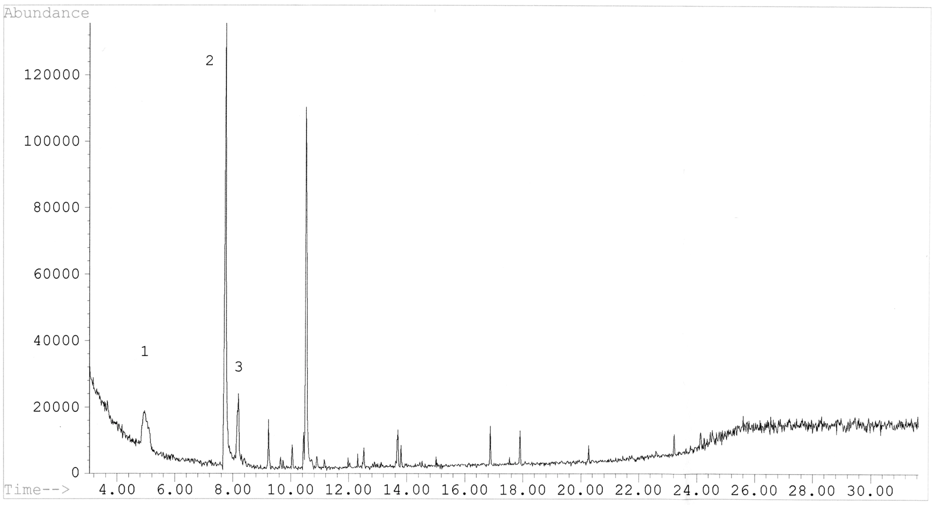

Figure 6: Total ion chromatogram (TIC) of run 7 : Oxidative treatment at 302°C, 10 s, 1: Phenol, 2: Benzoic acid, 3: Naphthalene

The effluent of this experimental run contains only traces of residual naphthalene.

In order to identify further degradation products of the partial oxidation a sample volume of 20 ml (run 9) was extracted with 20 ml of dichloromethane. The solvent was subsequently evaporated in a rotary evaporator and the residue re-solubilized in 1 ml dichloromethane.

A list of substances identified in this highly concentrated sample is given in Table 3.

Substance	Retention time [min]	Substance	Retention time [min]
Benzaldehyde	5.04	Phenylacetic acid	14.72
Phenol	5.55	Pelargonic acid	14.83
Hydroxy-benzaldehyde	6.92	Methylpropylphenol	16.67
Methoxyphenol	7.93	Phenyl derivatives	et seqq.
Naphthalene	10.71	Hydroxy-methoxy-benzaldehyde	17.42
Benzoic acid	14.30	Naphthalene derivatives	et seqq.
Methylbenzoic acid	14.68	Binaphthalene	33.35

Table 3: Naphthalene oxidation products of run 9: Partial oxidation at 375°C, 8 s

The results reveal that a number of different decomposition products is formed in trace amounts during partial oxidation of naphthalene. A complete quantification of all these substances is practically impossible and beyond the scope of the original working plan. Effluents of naphthalene conversion experiments will however be distributed to Partner 1 to conduct toxicity studies as agreed at the last Progress Meeting in Noordwijk.

3.2 Closed loop experiments with substrate from Partner 1 and 2

In line with the current Work Package closed loop experiments were conducted with the non-degradable residues received from Partner 1 and Partner 2. For each material 4 experimental runs were performed, studying the conversion under subcritical and near/supercritical conditions for a non-oxidative and oxidative treatment, respectively. The effluents were characterized in terms of the ratio of dissolved carbon to the total influent carbon and the contribution of carboxylic acids to the solubles. The effluent DOC was measured directly, while the influent carbon was calculated on the basis of the elementary analysis of the input material. As agreed, larger quantities of the effluents in the litre range were distributed to Partner 1 to run the methane units and close the loop.

The results of the closed loop experiments are depicted in Table 4.

Run No	T [°C]	τ [s]	Amount of H_2O_2	$DOC_{out, meas}$ / $TC_{in, calc}$ [%]	C_{acids} / C_{diss} [%]
11	385	29	0	39.5	12.9
12	320	43	0	27.4	6.1
13	413	8	2	9.3	84.2
14	350	15	2	7.5	59.3
15	398	8	2	7.2	112.7
16	289	10	2	15.1	2.1
17	372	50	0	35.4	3.4
18	331	60	0	11.7	12.7

Table 4: Closed loop experiments with solid residues from Partner 2 (run 11-14) and Partner 1 (run 15-18) on a carbon basis: P = 25 MPa, amount of H_2O_2 is given with respect to the stoichiometric demand, initial solid concentration: 1 wt%

It can be inferred that the degree of liquefaction under non-oxidative conditions (run 11,12,17,18) is markedly lower than in case of the first loop experiments, which resulted in conversions of about 60 %. This difference is especially pronounced in case of the material received from Partner 1. A possible explanation for this finding might be changes in composition of the solid residues.
The non-oxidative experiments yield a degree of liquefaction of 35-40 % at near/supercritical conditions, while the hydrolytic treatment at well-subcritical conditions yields conversions of 27 % (residues from Partner 2) and 12 % (Partner 1). Carboxylic acids amount to less than 13 % of the dissolved carbon.

In contrast, the oxidative destruction results in only slightly coloured, initially solid-free effluents. After a short time at room temperature the formation of tiny cords and subsequent precipitation of small amounts of solid material could be observed, which might be due to secondary reactions of reactive products. The residual dissolved carbon content is in the range of 7-15 % for both materials under oxidative conditions.
A significant difference can be observed with respect to the amount of carboxylic acids under subcritical and supercritical conditions. At well-subcritical conditions (300°C) only a small portion of the dissolved carbon can be attributed to carboxylic acids, which is probably a result of larger quantities of partially oxidized compounds. A temperature increase leads to an increase in selectivity of carboxylic acids, such that at supercritical conditions the majority of the dissolved carbon is present in form of acids (run 13, 15).

These results evidence that supercritical water oxidation is a suitable technology for efficiently converting biologically non-degradable materials to water-soluble substances and gaseous species within very short residence times. Also, the operating conditions can be optimized to selectively produce readily-degradable end products such as acetic acid.

3.3 Lignin oxidation experiments

Parallel to the work done on the HACCP study and the closed loop experiments, additional oxidative experiments with lignin have been executed. Lignin is of special interest since it serves as a model compound for real biological wastes containing ligno-cellulotic materials such as wheat straw and the non-degradable residues of Partner 1 and Partner 2.

For these experiments the operating conditions were systematically varied with respect to temperature, reaction time, and excess of hydrogen peroxide. The effluents are currently analysed for the dissolved organic carbon content and the concentration of carboxylic acids. Furthermore it is intended to subject selected samples to GC-MS analysis to study the effect of operating conditions on the product distribution by identifying major degradation products.

4 CONCLUSIONS / OUTLOOK

According to the work package descriptions experimental studies on the conversion of pure lignin and the treatment of biomass received from Partner 1 and Partner 2 have been performed. The closed loop experiments show that supercritical water oxidation technology can be successfully applied to convert the recalcitrant, non-degradable residues of the methane and the fibrobacter compartment. By supplying an excess of hydrogen peroxide the solid matter can be converted to water-soluble substances and gaseous species with a high selectivity of acetic acid formation under supercritical conditions. As agreed, several litres of effluent have been distributed to Partner 1 to close the loop.

The studies on the degradation of lignin, which serves as a model compound for ligno-cellulotic wastes, have been continued. Numerous experiments have been run for a comprehensive parameter study, varying temperature, residence time, and the amount of oxidant. The effluents of these runs are currently analysed in terms of the dissolved organic carbon content and the concentration of carboxylic acid. Further analyses of selected samples are planned to identify main degradation products depending on operating conditions.

As agreed on at the last Progress Meeting, studies have been conducted on the conversion of PCBs and PAHs under hydrothermal conditions. Based on a literature survey on the conversion of PCBs it can be concluded that supercritical water oxidation offers the opportunity to remove biologically persistent compounds like PCBs from the MELISSA cycle without producing more harmful reaction products, provided that the operating conditions are properly selected in the event that PCBs are present in significant amounts. In fact, supercritical water oxidation is successfully employed to decompose potentially hazardous substances.

Regarding the conversion of polycyclic aromatic hydrocarbons, experimental studies have been performed under non-oxidative and oxidative conditions. The non-oxidative treatment does not substantially transform naphthalene at the conditions applied, while the oxidative destruction removes naphthalene completely. Different analytical methods have been applied to identify an essential proportion of the dissolved carbon. Effluents of the naphthalene conversion under hydrothermal conditions will be provided to Partner 1 to run toxicity tests and conclude the issue of potential hazards in the decomposition of PCBs and PAHs.

5 LITERATURE CITED

---

1 Weber, R.; Yoshida, S.; Miwa, R.: PCB Destruction in Subcritical and Supercritical Water – Evaluation of PCDF Formation and Initial Steps of Degradation Mechanisms, Environmental Science & Technology **2002** (36), pp. 1839-1844

2 Hatakeda, K.; Ikushima, Y.; Ito, S.; Saito, N.; Sato, O.: Supercritical Water Oxidation of a PCB of 3-Clorobiphenyl Using Hydrogen Peroxide, Chemistry Letters **1997**, pp. 245-246

3 Anitescu, G.; Tavlarides, L.: Supercritical Water Oxidation Reaction Pathway and Kinetics of Polychlorinated Biphenyls, Proceedings of the 2001 Conference on Environmental Research **2001**, pp. 40-51

4 Sako, T.; Sugeta, T.; Otake, K.; Kamizawa, C.; Okano, M.; Negishi, A.; Tsurumi, C.: Dechlorination of PCBs with Supercritical Water Hydrolysis, Journal of Chemical Engineering of Japan **1999** (32), pp. 830-832