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TECHNICAL NOTE

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TECHNICAL NOTE: 4.8

DESIGN AND CONSTRUCTION OF A HYDROTHERMAL REACTION UNIT

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1 INTRODUCTION

Within the frame of the project “A total converting and biosafe liquefaction compartment for Melissa” a small-scale hydrothermal reaction unit was delivered to Ghent University, a Partner in the project. The main objective of this work was to physically couple the high pressure/temperature unit with the methanogenic reactor at Ghent University in order to directly process the indigestible biomass into the hydrothermal reactor and recycle the effluents back into the methane unit. This setup was designed to demonstrate the feasibility of implementing the hydrothermal reactor in a system consisting of biological compartments. That way the overall efficiency of the combined process with respect to the removal of solid biomass as well as the reliability of the setup can be investigated in future experiments.

The hardware was set-up in accordance with the contractual baseline. The design of the apparatus was presented at a Progress Meeting in Paris, November 22, 2004, and it was accepted by ESA. The first introduction to the equipment was given at Technische Universität Hamburg-Harburg, July 11-13, 2005, during a visit of co-workers from Ghent University. The hardware was delivered to Ghent University 31.08.-02.09.2005 along with the relevant manuals and a detailed instruction.

The main specifications of the demonstration plant are as follows:

- Maximum pressure: 300 bar
- Maximum temperature: 400°C
- Maximum throughput: 5 kg/h
- Initial solid concentration: 1-2 wt-%
- Reaction volume: 100 ml

A detailed description of the design of the apparatus including operating instructions is given in the following sections.

2 GENERAL LAYOUT

The high pressure/temperature reaction unit is designed as a fully continuous tubular reactor. The system consists of three separate lines upstream of the reactor. The first line is responsible for preheating and delivering the biomass suspension, while the second one can either process pure hot water or additional chemicals like hydrogen peroxide. These lines are mixed with a mixing tee directly upstream of the reactor. The third line can be used to introduce carbon dioxide to the system.

The pre-heaters and the reactor are manufactured as coils made of ¼” high pressure tubing, which are heated externally by resistance heating jackets. The reactor effluents are rapidly cooled down by passing a double-pipe heat exchanger operated with tap water. The effluents are subsequently passed through a gravity settler and a porous metal filter to retain solids before entering a spring-loaded backpressure regulator, by which the system pressure can be set to the desired value.

All pressure bearing parts are made of stainless steel (typically according to standard 316L). High pressure parts subjected to high temperature and corrosive environment (pre-heaters, reactor, and cooler) are made of corrosion resistant nickel alloy (Alloy 600). All peripheral devices like pumps and buffer and storage vessels as well as the data logging are mounted on a customized, mobile frame having a base area of 200 mm x 88 mm.

The plant setup is illustrated below.

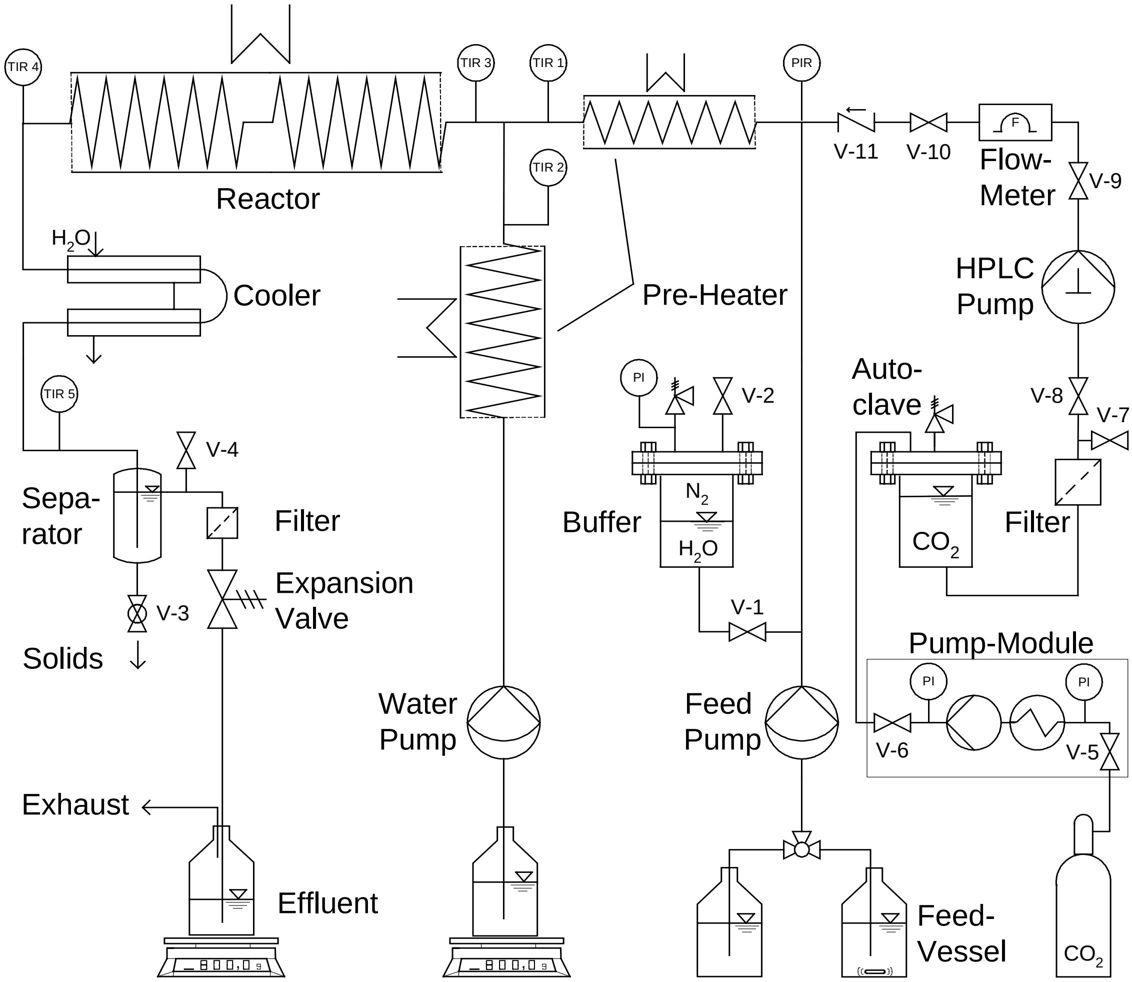


Figure 1: Flowsheet of the hydrothermal reaction unit

3 DETAILED DESIGN

Line 1, Feed line:

The feed is processed via a high pressure metering pump (LEWA, EK1) specifically designed for discharging biomass suspensions. The pump head is equipped with a PTFE sandwich membrane, which imposes two barriers between the fluid and the hydraulic oil. That way a proper operation is guaranteed even in case one of the membranes fails due to rupture. A

pressure gauge connected to the head measures and indicates the actual pressure in the membrane interspace. It shows no pressure reading in normal operation but indicates working pressure when one of the membranes fails. In that case the pump can still be run but the membranes should be replaced promptly.
The pump processes the fluid through double-ball valves at the suction and discharge side. The suspension can be delivered with a maximum flow rate of 5 kg/h at a maximum working pressure of 300 bar. Further information about the set-up, operation, maintenance, and trouble-shouting can be inferred from the manual.

The feed suspension is delivered in ¼” high pressure piping (OD: 6.35 mm, ID: 3.05mm, 316L) to the pre-heaters. Before entering the heating coils, the feed line can be connected to a 1 l buffer autoclave (Swagelok, 316L-50DF8-100, maximum pressure: 344 bar) via V1. This vessel serves the purpose of minimizing pressure fluctuations in the system, which might be due to the operation of the pumps and the opening of the backpressure regulator at higher flow rates. The buffer vessel can be filled with nitrogen through a supply line attached to V2. The supply line is equipped with a connector for nitrogen gas cylinders (SITEC, 729.9132, W 24,32 x 1/14“), by which the nitrogen can be transferred at the pressure in the cylinder. The autoclave is also equipped with a pressure gauge and a pressure relief valve for safety reasons.

For monitoring and recording the system pressure an electronic pressure transducer (STW A05, max. pressure range: 350 bar) is introduced into the feed line directly upstream of the pre-heaters. It converts the pressure input into an electronic signal (4-20 mA), which is processed by the data logging system described below.

The reaction unit consists of 4 segments, the feed pre-heater and the reactor, having 2 separate coils each. Each coil is made of 6 m high pressure piping, (OD: 6.35 mm, ID: 3.09 mm, Alloy 600), yielding a total reaction volume of 180 ml. Every section can be heated and controlled separately by a 1.5 kW ceramic heating jacket (Eichenauer, customized equipment). The heating jackets are enclosed by cylindrical insulations with a thickness of 4 cm (Horst, customized equipment) to minimize heat losses to the surroundings. The outer temperatures are measured by thermocouples (Conatex, T540K124AL500mmZ) placed between the surface of the coils and the heating jackets. The output signals are processed in temperature controllers (Eurotherm, 2132). The maximum allowable temperature of the jackets is 500°C.

The reaction temperature is measured with thermocouples (Conatex, T540K124AL500mmZ) which are introduced into the high pressure piping by means of corrosion resistant tee-connectors. There are 4 measuring points at different axial locations: TIR 1 after the pre-heater, TIR 3 after the mixing point, as well as TIR 4 at the outlet of the reactor and TIR 5 after the cooler. The temperature and pressure signals can be displayed and stored to files with the data logging system.

The effluents are cooled down in a self-made double-pipe heat exchanger. It is set up of 4 sections with a length of 0.7 m each. The inner pipe is made of ¼” high pressure tubing, yielding an outer heat transfer area of 560 cm^2. Tap water can be used as the heat transfer medium either in co-current or countercurrent mode. The medium is run in the annular gap between the inner pipe and the outer shell (stainless steel) of the exchanger.

In order to continuously process the biomass suspension, solids which might still be contained in the effluent stream should be retained before entering the backpressure regulator. For that purpose, a gravity settler and a filter unit have been implemented downstream of the cooler. The gravity settler is made of a high pressure cylinder (Swagelok, 316L-50DF8-100). The reactor effluents enter the separator at the top and flow downwards in a dip pipe (1/4”, stainless steel) in the centre of the cylinder. In the lower third of the vessel, the effluents stream leaves the dip pipe and the flow is directed in an upward motion in the gap between the inner pipe and the body of the cylinder. By that means, all particles having a sedimentation velocity higher than the upward flow velocity are separated and accumulated at the bottom of the vessel. To prevent re-entrainment of the solids, the separator is equipped with a ball valve (V3) and an outlet line. By opening V3 intermittently, the solids can be withdrawn from the autoclave.

In case the effluents bear larger amount of fines, a filter unit was placed after the gravity settler. The cylindrical shell of the unit contains a porous metal filter inlay to retain small particles. The cylindrical inlay is accessible by unscrewing the top of the unit and it can be easily removed and cleaned after every experiment.
After operation the separator can be cleaned by flushing it with tap water. For this, a hose can be connected to V4 after the separator. By reversing the flow in the settler, the cylinder is backwashed and particles attached to the surface can be washed out and removed via V3.

The expansion valve is designed as a spring-loaded backpressure regulator (Tescom, 26-1762-26-S). It holds the pressure in the system at a constant level by opening and by releasing any pressure exceeding the targeted value very quickly. The system pressure can be set freely by adjusting the spring tension through a handwheel. Subsequently, the liquid effluents leave the reaction unit and can be collected in vials placed on the bottom plate of the apparatus.

Line 2, Auxiliary line:

A separate line was implemented into the system to introduce additional chemicals or pure hot water to the feed. Like the feed line it is equipped with a high pressure metering pump (LEWA, EK1), which can discharge aqueous streams at a maximum flow rate of 2 kg/h. Due to the architecture of the pump head, e.g. its lower capacity and its small orifices, this pump is not suitable for processing solids.

The design of the auxiliary line is similar to the feed line. The aqueous influent is processed via ¼” high pressure piping (OD: 6.35 mm, ID: 3.05mm, 316L) to the pre-heater made of 6 m corrosion resistant nickel alloy (OD: 6.35 mm, ID: 3.09 mm, Alloy 600). The energy is supplied through a 1.5 kW ceramic heating jacket (Eichenauer, customized equipment), which is enclosed by a cylindrical insulation with a thickness of 4 cm (Horst, customized equipment). The temperature at the outlet of the pre-heater (TIR2) is measured with a thermocouple immerged into the stream and can be recorded by the data logging system. The two streams are mixed in a corrosion resistant tee-connector.

Line 3, Carbon dioxide:

The third line was designed for adding carbon dioxide as a supplementary means to lower the pH of the influents and to promote acid catalysis. The carbon dioxide is first liquefied and then processed with an air-driven pump to a storage cylinder, from which it can be delivered to the reactor by a HPLC-pump.

The cooler and the air-driven pump are housed in a pump module (NWA, PM-101). The module is equipped with a valve and a pressure gauge at the inlet (V5) as well as at the outlet

(V6). The pressure level at the outlet side is set by an integrated regulator, which controls the primary air pressure.

The liquefied pressurized carbon dioxide is delivered to a 300 ml storage cylinder (Swagelok, 316L-50DF4-300, maximum pressure: 344 bar). It can be sucked from the bottom of the cylinder by a HPLC-pump (Gilson, 305) at a maximum flow rate of 10 ml/min. Before entering the pump, the liquefied carbon dioxide passes a T-filter to protect the suction valve from particles. The line can be successively filled by shutting down the valve (V8) between the filter and the HPLC pump. Valve V7 was installed to release carbon dioxide and depressurize the line to ambient after the experiment.

The pump discharges the carbon dioxide to a mass flow meter (Rheonik, RHE 007). In order to determine and, if necessary, reset the zero point, the mass flow can be stopped by closing the valves before (V9) and after (V10) the meter. Detailed information about the operation of the HPLC-pump and the mass flow meter can be found in the respective manuals.

Since the mass flow through the carbon dioxide line is less than the flow through the feed line by an order of magnitude, the carbon dioxide passes a check valve (V11, Sitec, 720.4536) before being mixed with the feed. By this means, any disturbances on the carbon dioxide flow evoked from the stroke of the feed pump can be excluded.

All valves possess a pressure resistant body and are certified for the pressures applied in operation. They were purchased from Sitec and Autoclave Engineers. Connectors and fittings were purchased from Swagelok, Sitec, and Autoclave Engineers.

Data logging and temperature control system:

The hardware and software described below was developed and assembled by the “Forschungswerkstatt Elektrotechnik”, Technische Universität Hamburg-Harburg, under the reference number “FEW 08/05.

Table cabinet:

All temperatures are measured with NiCr-Ni thermocouples. Five thermocouples are needed to control the temperature of the five independent heating jackets. Another five temperature signals are measured and recorded at the outlets of the pre-heaters, after the mixing point, at the outlet of the reactor, and downstream the cooler.

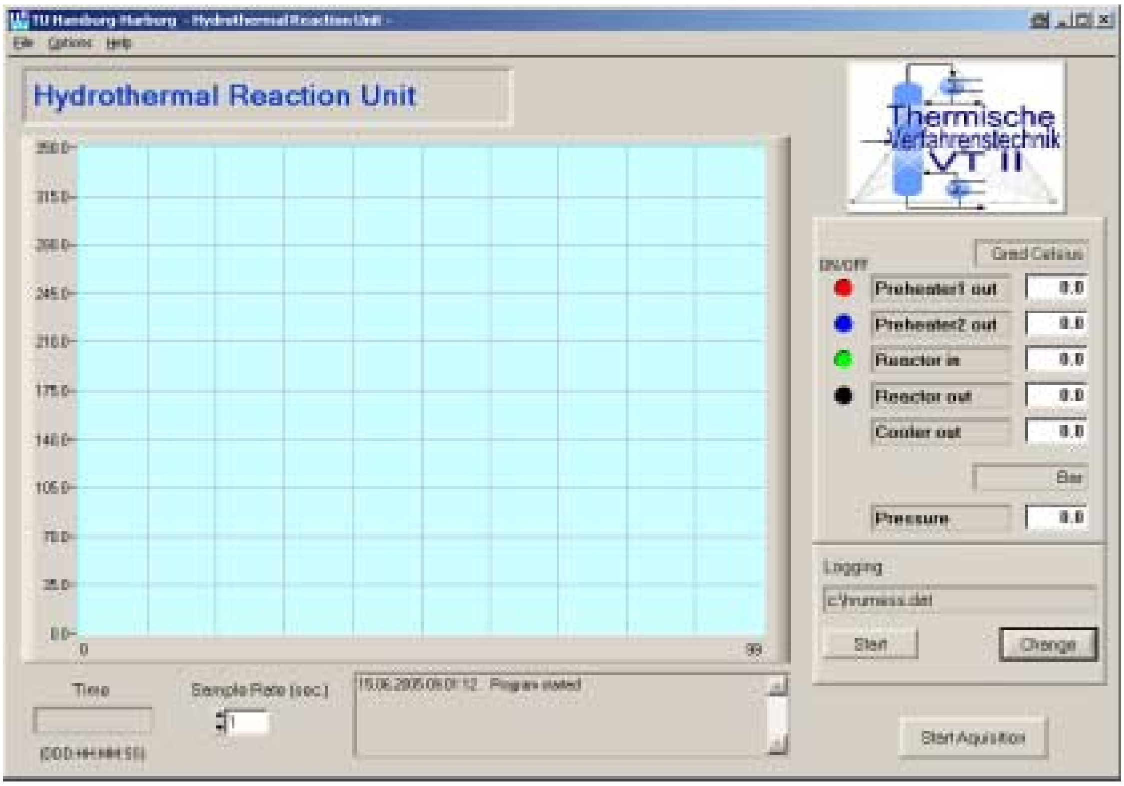
The output signals of the thermocouples and the pressure transducer are processed in a table cabinet. The cabinet houses 5 temperature controllers (Eurotherm 2132), each of which energizes a solid-state relay at the rear panel of the cabinet to power one heating jacket. The signals of the 5 temperature measuring points are processed and converted to digital signals in a universal bus module (NuDam 6018). Another module of the same type processes the signal of the pressure transducer (4-20mA). The two modules are connected to a converter (NuDam 6520) by a RS-422/485 interface, which provides a RS-232 output. The output signals can be transferred by a RS-232 (serial) interface at the rear panel to the computer.
The cabinet also houses a 24VDC power supply for the pressure transducer, the heating contactor, and fuses. A detailed description of the cabinet including wiring diagrams was provided to the operator along with the apparatus.
The cabinet is depicted below.

Figure 2: Picture of the table cabinet: front panel (left) and rear panel (right)
The front view shows the main switch, the on and the off button for the heating, the lever key for the acoustic alarm signal, the emergency shut off ("Not-Aus"), and the five temperature controllers
The rear view shows the sockets for the thermocouples (lower left: input signals for controllers; right: thermocouple input channels for data acquisition), the interface of the pressure transducer, the RS-232 interface, as well as the heat sinks of the solid state relays, the 230 V sockets, and the fuses

Data acquisition software:

The acquisition software “HRUMESS” was developed with the software LabWindows\CVI Version 7.1.0(306) from National Instruments. The program was developed and successfully run with the operating system Windows 2000 Professional, SP 4. The respective hardware, a commercial personal computer, with pre-installed acquisition software and operating system, was delivered to Ghent University and tested on site.

The software enables the user to indicate and record temperature and pressure signals. All configurations, e.g. the sample rate, the RS-232 parameters, and the parameters for the different channels (like gain, set-off, and range), can be performed with the programme. After starting “hrumess.exe”, the user gets access to the main window illustrated below.



Preheater1 out 0.0
Preheater2 out 0.0
Reactor in 0.0
Reactor out 0.0
Cooler out 0.0
Pressure 0.0
Logging c:\hrumess.dat
Sample Rate [sec.] 1
15.06.2005 09:01:12 Program started

Figure 3: Main window of the program „HRUMESS“

The first 4 temperature values can be displayed graphically by actuating on the “On-Off” button. The temperature after the cooler and the pressure value are not displayed graphically.

The user can choose a logging file and start the acquisition from here. The main window also includes a smaller window displaying status and error messages. The value for the sample rate and the actual time can be set in the main window, too. All other settings are done in the “file” and “option” menus.

A detailed description of the acquisition software was included in the hardware manual of the cabinet.

4 PICTURES OF THE APPARATUS

Figure 4: Front view of the apparatus

Figure 5: Rear view of the apparatus

5 OPERATING INSTRUCTIONS

The following instructions are based on the assumption that the starting conditions are as follows:

- The apparatus is completely emptied and at ambient pressure
- All valves are closed
- The backpressure regulator is completely opened
- All devices are connected and have the respective supplies (electricity, cooling water, carbon dioxide, pressurized air)
- The buffer autoclave is filled with nitrogen
- The system is tight
- All pieces of equipment run properly

Start up (without CO_2):

1 Switch on the computer and the table cabinet (main switch), start the acquisition program
2 Turn on the feed pump and the water pump and fill the apparatus with water
3 Set the desired pressure by acting on the backpressure regulator
4 Open V1 to connect the buffer autoclave (make sure the that the reactor pressure is not significantly lower than the pressure in the vessel in order to prevent loss of nitrogen)
5 Check the mass flow; if necessary, adjust the pump stroke
6 Programme the setpoint values of the temperature controllers; turn on the heaters (check water supply of the cooler)
7 Wait until the system is at stationary conditions (constant temperature)
8 Change the feed flow from pure water to feed suspension (preferably with a three-way valve, make sure that any air, which might be initially present in the suction line, has been discharged before, the pump is not designed to discharge large quantities of gas against operating pressure)
9 Conduct the experiment; carefully open V3 after a while to check whether solids are present in the effluents; in case there are, open V3 intermittently to withdraw solids (use unbreakable container)

Shutdown (without CO_2):

1 Switch to pure water and flush the reactor at operating temperature for 10-15 minutes
2 Turn off the heaters; wait until the system has cooled down
3 Close V1
4 If necessary, withdraw remaining solids from the separator
5 Depressurize the reaction unit with the backpressure regulator
6 Turn off the pumps
7 Switch off the computer and the cabinet
8 Backwash the separator via V4
9 Remove and check porous metal inlay of the filter

Operation with CO_2:

With regard to the feed and the auxiliary line, the procedure is the same. Some additional steps have to be carried out when using carbon dioxide.

Start up (CO_2):

1’ Parallel to point 1 of the above checklist switch on the mass flow meter and the HPLC-pump; plug in the pump module and open V5 (inlet valve of the pump module), the cooler will start to liquefy the CO_2
After 10-15 minutes open V6, the storage cylinder will be filled with CO_2; carefully increase the air pressure (black knob in the middle of the front panel) to about 150 bar (pressure gauge at outlet side), if the air-driven pump is continuously operating without any noticeable increase in pressure, the CO_2 in the module has not been liquefied yet, in this case decrease air pressure and wait a couple of minutes before trying again

The next steps should not be carried out before step 3 of the above list (pressurizing the reaction unit)

2’ Open V8, V9, and V10

3’ Programme the desired flow rate and start the HPLC-pump

4’ After five minutes stop the pump and close V9 and V10, check if the value indicated by the flow meter approaches zero, if necessary, reset the zero point of the flow meter; open V9 and V10 and restart the pump

Shutdown (with CO_2):

1’ When flushing the reaction unit with pure water, turn off the HPLC-pump, plug out the pump module and decrease air pressure, close V8 and V5

2’ Carefully open V7 and depressurize the section between V5 and V8 by releasing carbon dioxide through V7

3’ When the CO_2 supply is at ambient pressure (check pressure gauge at the outlet of the pump module) close V7 and V6

4’ The section between V8 and V11 will be depressurized via the check valve V11 when expanding the reactor through the backpressure regulator, close V9 and V10 once the system is at ambient pressure

Possible failures during operation and respective measures:

I Pressure decrease:

A significant decrease in pressure might most probably be due to a pump failure or problems with the backpressure regulator.

- Turn off the heaters, close V1 and V8 (if applicable), increase stroke of the pumps
- Shut down the system
- Refer to the trouble-shouting section and eliminate cause for failure

II Pressure increase:

A constant pressure increase might occur as a result of an increased flow resistance (deposition of solids, plugging). The system pressure is however limited to a maximum of 300 bar by the internal overflow valves of the pumps.

- Decrease stroke of the pumps
- Shut down the equipment and solve the problem

III In case of an emergency:

If possible, switch off electronic devices (“Not-Aus” switch) and put yourself at a safe distance from the apparatus until the danger has passed.

6 TROUBLESHOOTING

Failure	**Possible causes**	**Alternatives**	**Symptoms**	**Remedy**
No pressure build-up / drastic pressure decrease during operation	Pump(s) are not delivering fluid	Power Supply	Motor is not running	Check installation; consult electrician
		Gas in pump head	Motor running but no discharge of fluid	Increase stroke to discharge air; apply pressure to suction side; tighten fittings
		Solids stuck in pump head		Flush with water or organic solvent; remove, disassemble and clean valves
	Defective backpressure regulator	Solids trapped in regulator	No or limited pressure build-up; large fluctuations	Flush with water; disassemble and clean
		Worn out seat or shaft		Replace parts
Pressure increase during operation	Solid deposition / plugging	Deposition in reactor/cooler	Increasing pressure/ knocking sound of pump	Chemical/mechanical cleaning of pipes
		Deposition in filter		Remove and clean filter

This is just a compilation of possible problems which might be encountered during operation. The equipment was tested at TUHH and the faultless operation was demonstrated at Ghent University. In case of errors concerning single parts of equipment, the operator is referred to the respective manuals for troubleshooting.

In case of leakage the user is strongly reminded to **never attempt to tighten fittings at pressure-bearing parts under any circumstances**.

7 PARTS LIST (MAIN ITEMS)

Item	**Amount**	**Description**	**Manufacturer**
Pumps			
Feed Pump (5 kg/h)	1	Lewa EK 1	Lewa
Auxiliary Pump (2 kg/h)	1	Lewa EK 1	Lewa
CO_2 Metering (10 ml/min)	1	Gilson 305	Gilson
CO_2 Pump Module	1	NWA PM-101	New Ways of Analytics
Pressure Vessels			
Buffer Autoclave (1 l)	1	316L-50DF8-100	Swagelok
Separator (1 l)	1	316L-50DF8-100	Swagelok
CO_2 Storage (300 ml)	1	316L-50DF4-300	Swagelok
Heaters			
Ceramic Heating Jackets	5	1500 W, customized	Eichenauer Heizelemente
Insulation			
Insulation Jackets (4 cm BCTEX)	2	L: 300 mm, customized	Horst
Insulation Jackets	3	L: 350 mm, customized	Horst
Piping			
Reaction Pipe	30 m	6.35x1.63, Alloy 600	S+D Spezialstahl
Cooler (Inner Pipe)	3 m	6.35x2.11, Alloy 600	J&J Ethen
Other ¼” Pipe	6 m	6.35x1.65, 316L	Dockweiler
Valves			
Backpressure Regulator	1	Tescom 26-1762-26-S	Tescom Europe

8 HAZARD ANALYSIS OF THE HYDROTHERMAL REACTION UNIT

Introduction:

The HACCP concept (Hazard Analysis Critical Control Points) is a method to reveal, eliminate (or reduce) potential hazards, and to control their consequences. It was originally developed in food industry in the 1960s to manage food product safety, but it has been gaining increasing attention and applications in other branches, e.g. the space industry, in the past decades. Being an instrument to assure safe operation of plants and fabrication of safe products, the concept of HACCP interfaces quality management methods like FMEA (Failure Mode Effect Analysis).

In the context of HACCP, a hazard is defined as any existing or potential condition of an item that can result in a mishap. In this sense, such a condition can be associated with the design, fabrication, operation, or the environment of the item. The hazard itself is not an event but a potential threat to the safety of the system. It is a prerequisite for the occurrence of a hazard scenario, which is initiated by an event (i.e. cause). A hazard scenario reflecting the propagation of events is exemplified in Figure 6.

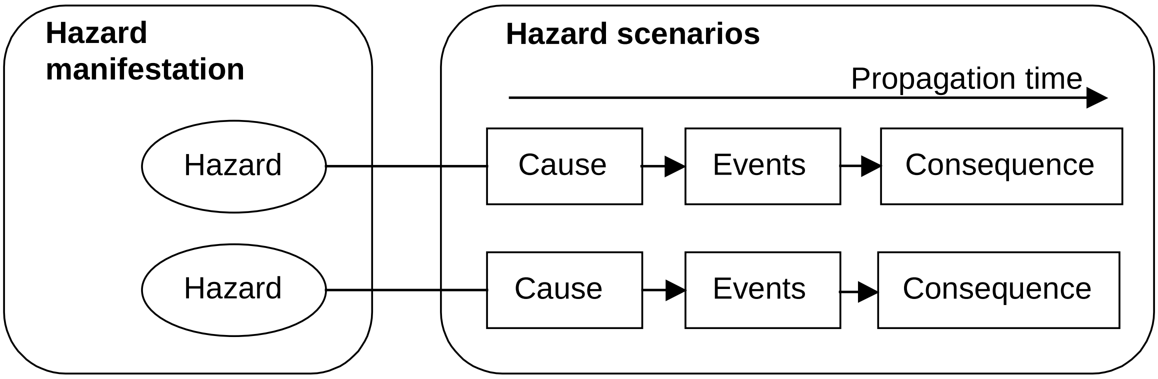


Figure 6: Hazard scenario; sequence of events leading from the initial cause to the unwanted safety consequence

Due to the presence of specific hazards in the technical design, operation or environment of the system (hazard manifestation), an initiating cause can set off a series of events leading to more or less severe safety consequences with increasing propagation time. Events are associated with the occurrence of observable symptoms, meaning that there is a time span between the occurrence of the cause and the detection of the symptoms (detection time). Accordingly, the time to react to the activated hazards and to take countermeasures is defined as the time span between the detection of the symptoms and the occurrence of consequences.

One single hazard can lead to several different consequences by the effect of different causes. The collection of all possible scenarios originating from the same hazard is expressed by a hazard tree. Analogously, different hazards can lead to the same consequence. The compilation of all hazards resulting in the same consequence is depicted by means of a consequence tree. Figure 7 shows the two concepts.

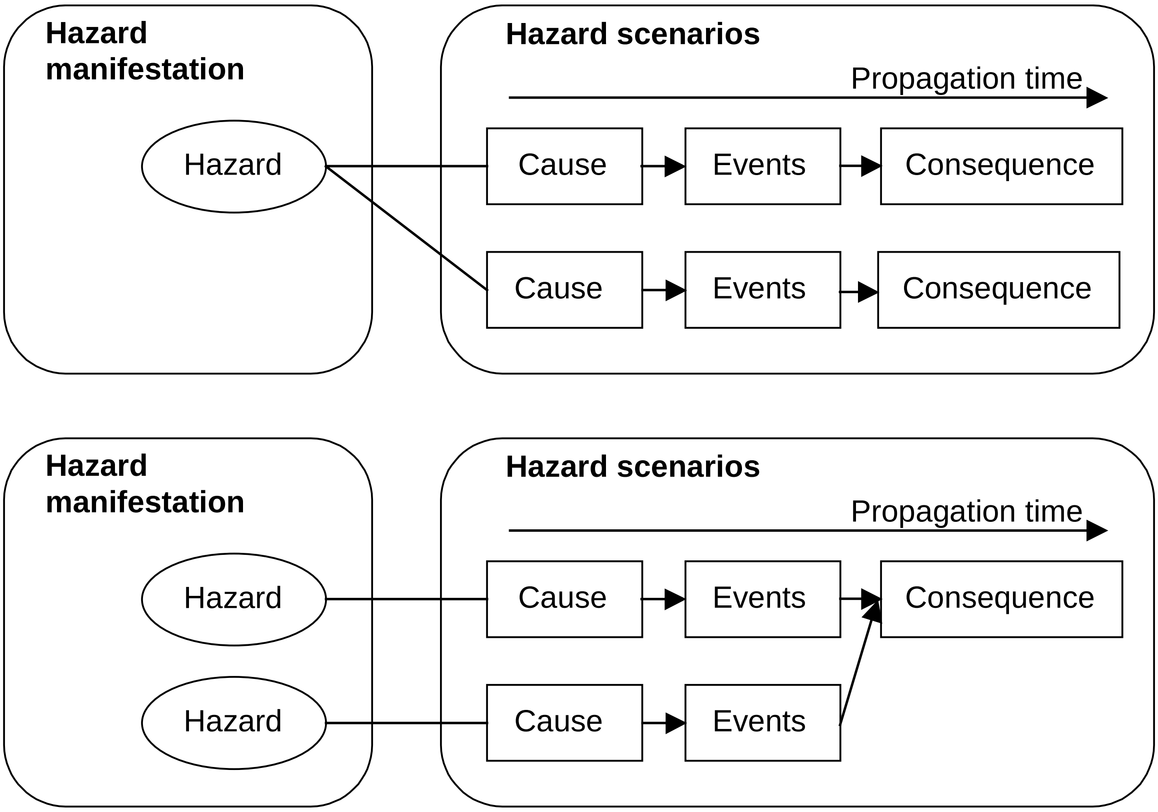


Figure 7: Examples of a hazard tree (top) and a consequence tree (bottom)

According to the schemes illustrated above, different approaches can be employed to reduce hazards and thus increase the level of safety of a system. The most sustainable way to reduce hazards is to eliminate them. This is, however, not always possible since some hazards, e.g. severe operating conditions, are inherent to the system and cannot be avoided without completely changing the process. In case hazards cannot be eliminated the attempt is made to minimize them, meaning that the level or amount of specific potentially safety threatening system characteristics is reduced.

Another way of increasing the level of safety is to control the hazards. Hazard control is either accomplished by preventing the occurrence or by reducing the likelihood and mitigating the effects of events. Hazard control can therefore impact on different parts of the hazard scenario. It can aim at excluding the occurrence of the initial cause (elimination of event), or at interrupting the propagation of events. This can either be accomplished by impacting on the link between cause and event or by preventing the propagation from events to consequences (mitigation of effects).

The different methods of hazard reduction are illustrated schematically in Figure 8.

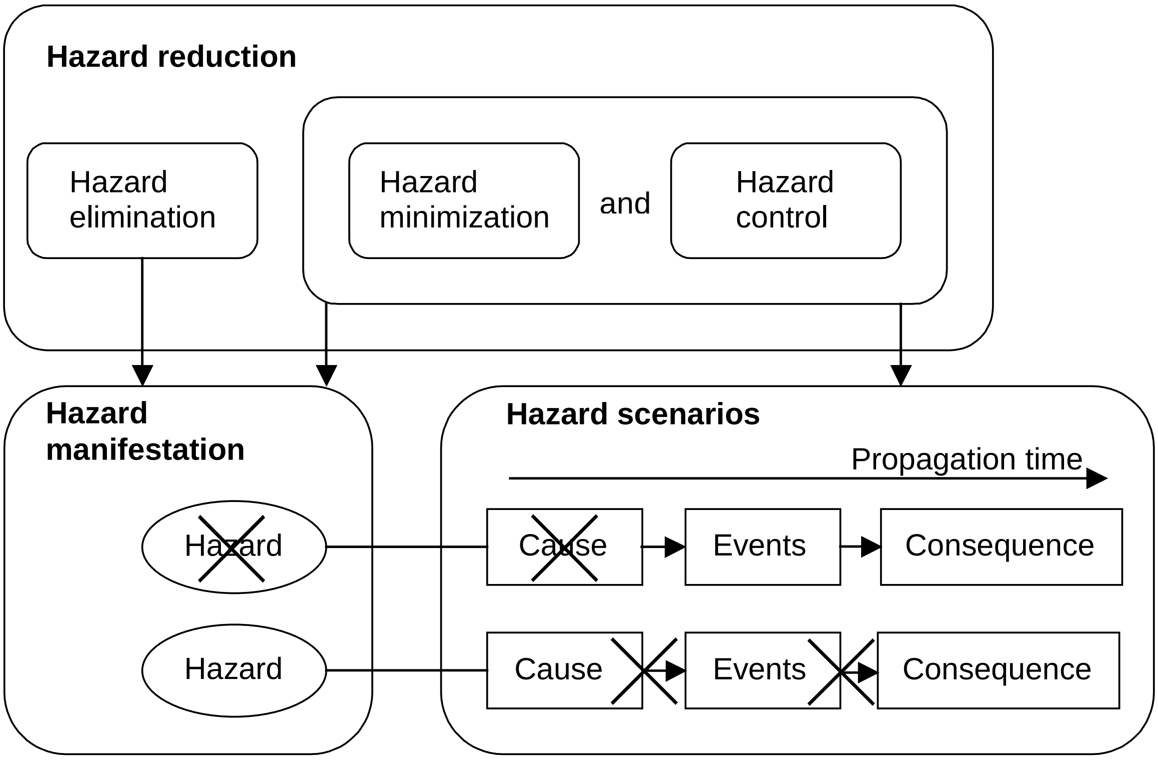


Figure 8: Hazard reduction; elimination and minimization of hazard, prevention of event, interruption of event propagation

Hazard analysis following the HACCP method is a general approach, which can in principle be applied to all potential hazards and processes. A hazard, being a potential condition possibly resulting in a mishap, may be of biological, chemical, physical, thermodynamic, or any other nature. Important biological hazards are micro-organisms, especially those having a pathogenic or carcinogenic effect on the human body. Toxicity, corrosiveness, flammability, and asphyxiant properties present major chemical hazards. High temperature and pressure conditions are counted among thermodynamic hazards.

The primary objectives of hazard analysis are firstly to assess the level of safety of a system in a deterministic way and secondly to increase the level of safety through subsequent hazard reduction. Following a short description of the HACCP process in general, the application of a hazard analysis to the process under consideration, the continuous treatment of plant biomass in near-critical water, is given in the next section.

Hazard analysis process:

Hazard analysis according to the HACCP method is a four-step iterative process comprising nine tasks. The four-step approach with the associated tasks is illustrated in Figure 9.

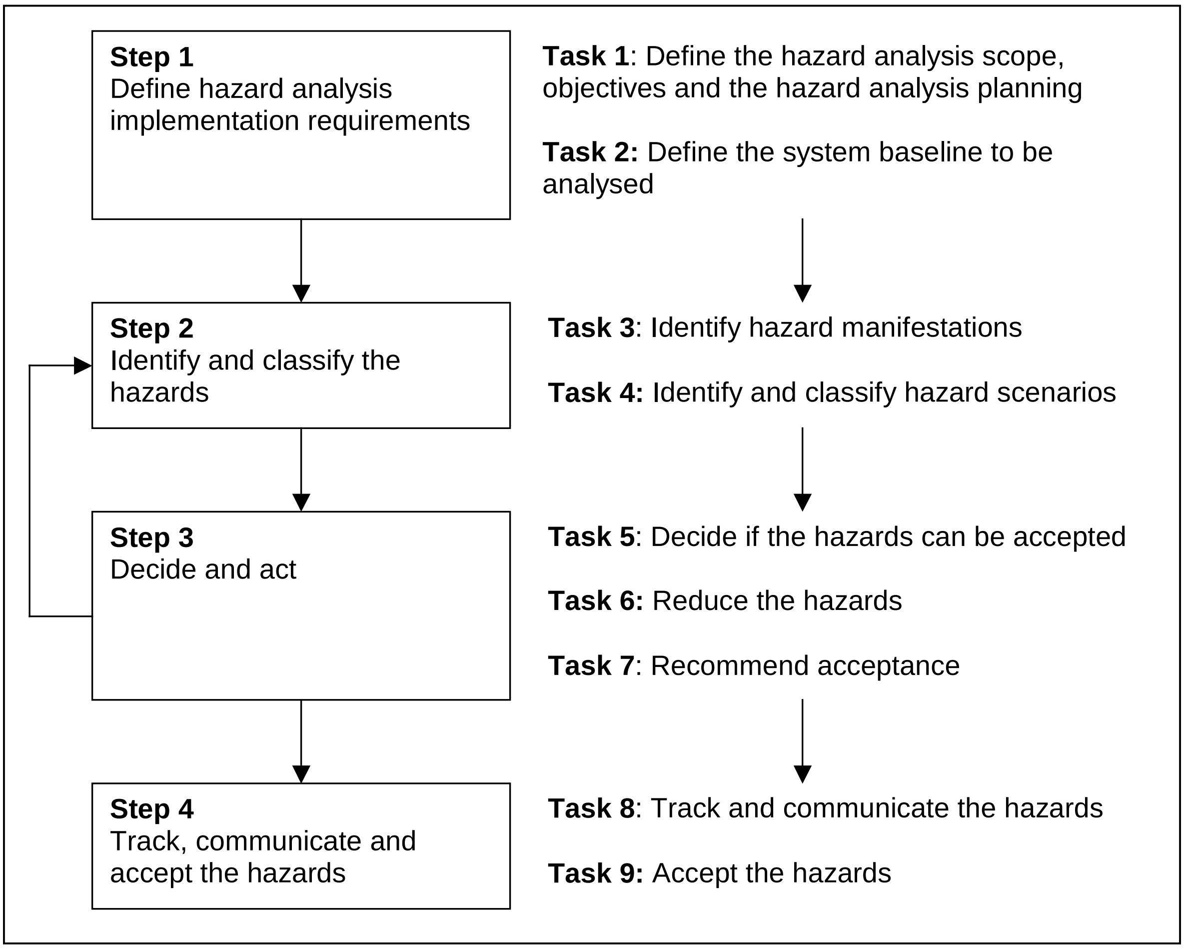


Figure 9: The hazard analysis process, shown are the four steps comprising nine tasks

The tasks associated with step 1 serve the purpose of laying the baseline for the analysis. The scope, objectives, and the planning are established (task 1). Furthermore, an exact definition of the system to be analysed is provided (task 2).

Step 2 comprises a thorough look at the system. The purpose of this step is to identify hazard manifestations (task 3) and the respective hazard scenarios originating from the manifestations (task 4). Task 4 also includes a classification of the scenarios according to the severity of the consequences.

Based on the output of the preceding steps decisions have to be made whether the hazards can be accepted or not (task 5, step 3). In case of rejection, the hazards are subjected to reduction (task 6). This step causes the iterative character of hazard analysis, since the results of hazard reduction constitute a new input to step 2 and alter the scenarios identified before. Following decision (acceptance or rejection) and action (hazard reduction) a recommendation for acceptance is made.

The tasks associated with step 4 include a periodical review of the hazards to reveal changes and, if applicable, update the scenarios and the hazard reduction (task 8). The effects of reduction measures on the system performance are verified. The hazard analysis process concludes with a formal acceptance of the residual hazards (task 9).

Analysis of the hydrothermal liquefaction:

Task 1: Definition of scope and objectives:

The scope of the analysis is to assess the level of safety of an already finished demonstration plant. The concept of several “hazard analysis cycles” over the project’s duration would have required the implementation of hazard analysis at earlier stages of the project, e.g. during planning and erection, and does therefore not apply. The project was to deliver a hydrothermal reaction unit to Partner 1 of the MAP-project in order to couple it to the methane reactor at Ghent University and demonstrate the feasibility and efficiency of the overall cycle. Partner 1 is responsible for operating the equipment in accordance with national and European regulations.

The scoring schemes for the severity of safety consequences were adopted from the proposition by ESA. The system was designed for ground operation only. Hence, consequences concerning flight operation do not apply. The categorization of safety consequences with respect to severity is given below.

Category	**Severity**	**Severity of safety consequence**
I	Catastrophic	Loss of life, life-threatening or permanently disabling injury or occupational illness; Loss of system; Severe detrimental environmental effects
II	Critical	Temporarily disabling, but not life-threatening injury or illness; Major damage to system; Major damage to public or private property; Major detrimental environmental effects
III	Marginal	Minor injury, minor disability, minor occupational illness; Minor system or environmental damage
IV	Negligible	Less than minor injury, disability, occupational illness; Less than minor system or environmental damage

Task 2: Definition of system baseline:

The system to be analysed is a hydrothermal reaction unit, which is run by qualified and trained personal for scientific purposes. The specifications, design, and operation of the system are described in detail in the preceding chapter. It was designed and built for application in a ground facility having all installations and infrastructure necessary for operation. The system was delivered to Ghent, Belgium, and is currently operated in a laboratory at Ghent University.

A conceptional presentation of the process is depicted in Figure 10 in form of a flow diagram.

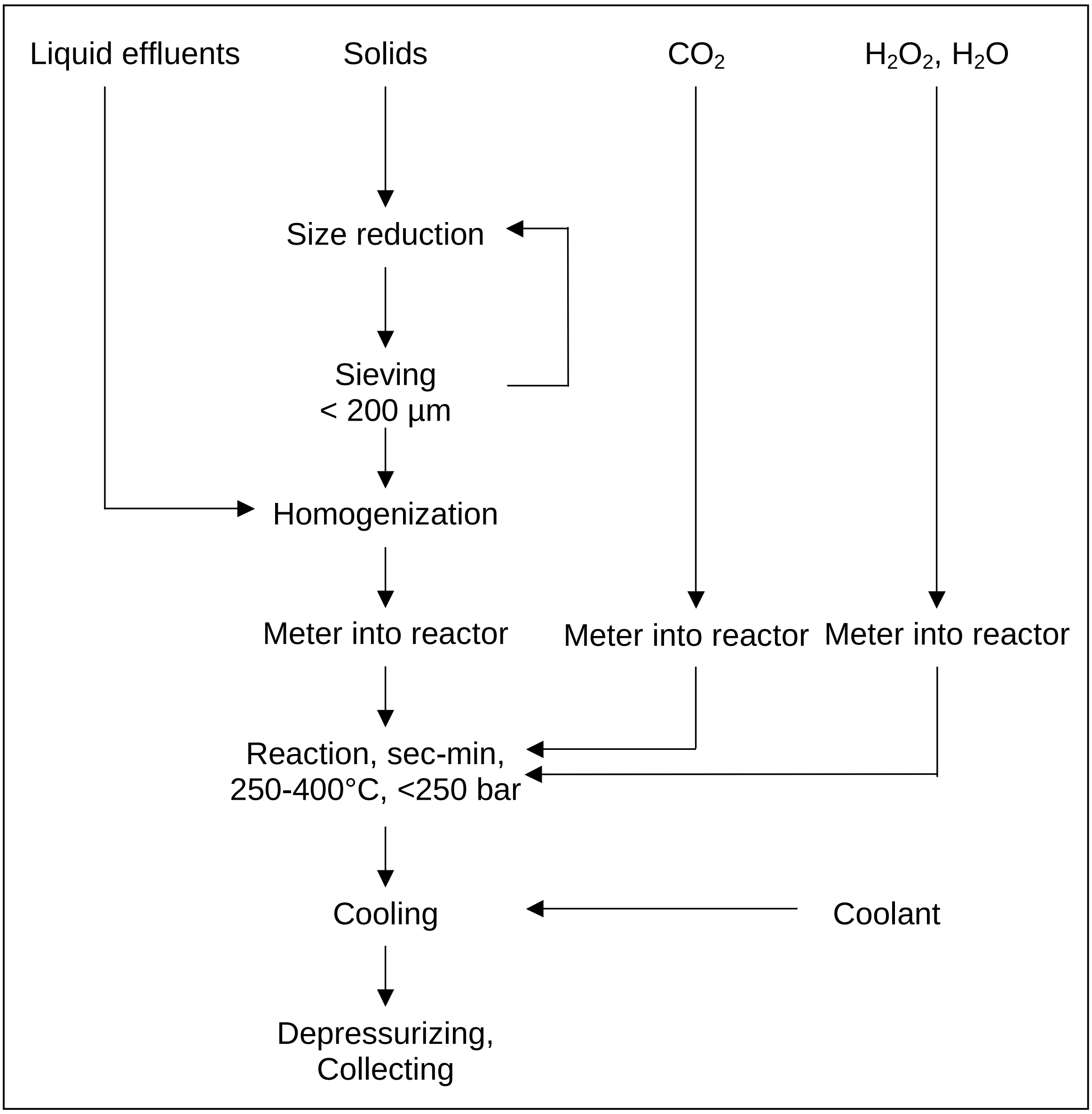


Figure 10: Process flow diagram of the hydrothermal treatment

Task 3: Identification of hazard manifestations:

Different generic hazards might be applicable to the hydrothermal treatment process. In the following, the hazards are discussed according to their nature.

Biological hazards:

Biological hazards do neither constitute a threat to the hydrothermal system itself nor to any subsequent biological compartment. The hydrothermal treatment is a thermo-physical system which is not affected by micro-organisms of any kind. In addition, it could be shown that the hydrothermal effluents are completely sterile, meaning that any biological hazards at the input like pathogenic bacteria or viruses are removed by the heat treatment. In this sense, the hydrothermal process adds a barrier and a safety switch and increases the biosafety of the overall set-up.

Chemical hazards:

In principle, several chemical hazards might be applicable to the system. Pressurized gases like carbon dioxide and nitrogen exhibit asphyxiant properties. Hydrogen peroxide can be harmful, corrosive, and fire-promoting and it bears the risk of explosion with substances listed in the respective material safety data sheet. Some parts of the equipment, e.g. the electrical installations, are flammable and dangerous fumes could be released during combustion.

These hazards are, however, not specific to the system under consideration, but they are generic hazards, which are associated with the material properties of the chemicals used. The apparatus was designed and built for operation in a ground facility, implying that the chemicals intended for use can be handled safely by the respective laboratory. The system was neither specified as explosion- nor as flameproof. These hazards will therefore not be examined any further.

The conversion of chemical compounds in high temperature water might be a hazard specific to the system. In this context, the possible transformation to degradation products having a toxicity higher than that of the input material needs to be considered.

Thermodynamic hazards:

The conversion of plant biomass in sub- and nearcritical water is a process applying high temperatures and pressures. Consequently, high temperatures and pressures are conditions which can be identified as specific hazards to the system to be analyzed.

In summary, the transformation to degradation products having an increased toxicity to micro-organisms and the operating conditions themselves, e.g. the application of elevated temperatures and pressures, are system specific hazards. A list of the hazard manifestations is given below.

Hazard manifestation list		
Operation	**System**	**Hazard manifestation**
Ground operation	Hydrothermal reaction unit	Treating of biomass suspension at a pressure of up to 25 MPa Treating of biomass suspension at a temperature of up to 400°C Converting biomass constituents to products showing detrimental effects on micro-organisms

Task 4: Identification and classification of hazard scenarios:

The hazard manifestations identified above can lead to safety consequences in case they are triggered by causes. All causes, which might initiate hazard scenarios, as well as the corresponding propagation of events and possible consequences need to be determined in order to assess the level of safety of the system. The severity of the consequences has to be evaluated according to the proposed scoring scheme. Also, an estimation of detection time and reaction time is required for each propagation of events.

As mentioned before, the system to be analyzed has already been finished. Different methods of hazards reduction have been applied to decrease the residual hazards to an acceptable level. Hence, it is not possible to identify and classify hazard scenarios without taking into account the hazard reduction already incorporated.

The hazard manifestations to be discussed cannot be eliminated. The severe operating conditions in terms of pressure and temperature are required to treat the biomass at the targeted thermodynamic state. Regarding the possibility of producing harmful by-products, this concern is mainly caused by the high reactivity of water at elevated temperatures and pressures. This is, however, a desired property in order to convert biomass which cannot be degraded by alternative means.

A list of applicable hazard scenarios is given in the following.

Hazard scenario list for ground operation I				
Hazard manifestation	**Cause – Events - Consequence**	**Consequence Severity**	**Observable Symptoms**	**Propagation and reaction time**
Water at highly reactive conditions	Significant level of unwanted precursors – conversion to harmful products – detrimental effect on micro-organisms	For HT unit: negligible For biological units: negligible (based on data so far), might be catastrophic if applicable	Slowed or negative growth and activity of micro-organisms	Ptime: hrs – days Rtime: N/A

The system was designed to treat plant derived biomass. In the course of the project, different types of biomass, including the model waste specified by ESA, recalcitrant solid residues obtained from the methane unit of Partner 1, wheat straw as well as model compounds like cellulose and lignin could be successfully converted. The effluents of the hydrothermal treatment exhibited a much increased bioavailability, as shown by series of fermentation tests conducted by Partner 1. Inhibitory or even toxic effects on the micro-organisms employed have not been detected in these experiments. Based on the experiences so far, the likelihood of the formation of harmful by-products in larger quantities is so low that the consequence severity can be rated as negligible. The toxicity analyses were, however, performed on a comparatively small amount of effluents from the hydrothermal unit. For long term closed loop systems the effects have not been studied in detail so far. This objective can now be accomplished by physically coupling the hydrothermal and the methane unit.

In addition, the risk of producing harmful products can even be decreased further by hazard reduction. The analysis of the influent material constitutes a critical control point of the process. By analyzing the influents, unwanted compounds like PCBs, whose degradation products might exhibit a toxicity higher than that of the PCB itself, could be identified. Accordingly, the operating conditions could be adjusted to higher temperatures and prolonged residence times to guarantee a complete destruction and mineralization of all substances.

The treatment of unwanted, biologically persistent compounds like PCBs, which are not present in significant amounts in the wastes specified by ESA, was not envisaged with the system to be analyzed. Another suitable way of hazard reduction would therefore be to prevent the occurrence of potentially critical components in the influents and solely treat plant derived biomass.

Hazard scenario list for ground operation II				
Hazard manifestation	**Cause – Events - Consequence**	**Consequence Severity**	**Observable Symptoms**	**Propagation and reaction time**
Water at elevated temperatures and pressures	Excessive pressure, temperature, material failure – formation of fissure – escape of hot fluid/vapor	For HT unit: Negligible For operator: Negligible to critical	Pressure loss, release of steam	Ptime: sec Rtime: N/A
	Inexpert mounting of fitting – rupture – escape of hot fluid/vapor	For HT unit: Negligible For operator: Negligible to critical	Pressure loss, release of steam	Ptime: sec Rtime: N/A
	Breakdown of coolant supply – increasing effluent temperature – damage of system components, release of hot fluid	For HT unit: Negligible For operator: Negligible	Increasing effluent temperature	Ptime: min Rtime: min
	Deposition of solids, plugging – increasing pressure – breakdown of continuous operation	For HT unit: Negligible For operator: Negligible	Increasing pressure (up to 30 MPa)	Ptime: min - hrs Rtime: min - hrs

The scenarios identified above essentially lead to the same consequence, the release of hot water. The likelihood of the occurrence of events has been reduced to a minimum level by different methods of hazard reduction.

The occurrence of improper operating conditions in terms of excessively high pressures and temperatures is prevented by safety installations. The apparatus is equipped with pressure relief valves, which are activated at a pressure of 30 MPa. In addition, the pumps possess internal overflow valves, which release the hydraulic oil to the oil reservoir at pressures exceeding 30 MPa, meaning that no further fluid is processed into the apparatus. The occurrence of excessively high temperatures is prevented by a safety shut-down of the heating jackets. The maximum allowable surface temperature is set to a value of 500°C. At temperatures exceeding this limit, the power supply to the jackets is disconnected and an acoustic alarm is set off. The reactor was made of a corrosion resistant nickel-based alloy (Alloy 600) to assure long-term operation and minimize the risk of fissures due to corrosion.

The initiation of events due to inexpert mounting can be excluded. The apparatus has been assembled by trained, professional personal. It was tested at the maximum allowable operating conditions and did not show any signs of failing. In order to maintain this state, any future modifications to the apparatus should exclusively be performed by professional personal after approval.

In case of a breakdown of the coolant supply, the effluent temperature starts rising. This is an observable symptom, since the temperature signal is displayed. The reaction time is sufficiently long to interrupt the propagation of events, e.g. by switching off the heating and adjusting the flow rate of the pumps.

In case of solid deposition/plugging the operating pressure rises due to the increased flow resistance. This is a creeping rather than a sudden process. Plugging will eventually lead to the consequence that no further fluid is delivered to the apparatus and that the continuous operation breaks down. This neither poses a threat to the equipment nor to the operator. The system has to be shut down and needs to be cleaned chemically/mechanically before putting it into operation again.

Despite the fact that the occurrence of leakages and fissures has been suppressed to a minimum, additional hazard control should be applied during operation in order to minimize the severity of possible consequences for the operator. **The most important measure to mitigate the effect of such unlikely events is to protect the human body from exposure to hot, pressurized water. Personal protective clothing is therefore mandatory when operating the equipment.** Assuming that the respective protective devices are applied and that sensitive parts of the body are protected, the consequences for the operator should be negligible. They might, however, be more critical in case the applicable safety regulations are not taken into account.

Task 5: Decision if hazards can be accepted:

Based on the determination of possible hazard scenarios and the evaluation of their severity, Partner 4 is of the opinion that the system can be operated at a very high level of safety and that the residual hazards can be accepted.

9 CONCLUSIONS

A hydrothermal reaction unit was designed, constructed, and delivered to Partner 1 of the project in accordance with the work package descriptions. The main purpose of this hardware is the physical coupling of thermal and biological systems in order to demonstrate the feasibility of a complete and biosafe conversion of solid biomass in a closed loop system. The design of the hardware was accepted by ESA at the Progress Meeting in Paris, November 22, 2004. The operator, Partner 1, was introduced to the equipment in Hamburg, July 11-13, 2005 before final delivery to Ghent University, August 31 – September 2, 2005. A hardware acceptance review was successfully conducted at Ghent University, March 9, 2006.

The level of safety of the system was assessed by a hazard analysis following the HACCP method. The analysis shows that the hardware can be operated at a very high level of safety and that the residual hazards are in an acceptable range.