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Design, Commissioning And Start-Up of a New Hydrothermal Liquefaction Continuous Pilot Unit

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Hydrothermal liquefaction (HTL) has been demonstrated to be an effective emerging technology for the conversion of various biomass slurries into valuable biofuels and bioproducts precursors. Many studies have been carried out in batch laboratory-scale apparatus, an effective technique to understand the conversion process applied on several wet materials, from algae to organic wastes and lignocellulosic streams. On the other hand, some examples of continuous system have been implemented and tested worldwide as first step for the industrial scale-up of the technology. This work focuses on the development from the design to the start-up and commissioning of a new continuous HTL unit, established in RE-CORD laboratories. The plant is capable of converting 1-2 kg/h of slurry at about 10 wt.% of biomass to water ratio. The hydrothermal conversion unit comprises a high−pressure slurry feeder, an indirectly heated plug flow reactor, a cooling system, a pressure let-down system and liquid-gas separator. The reactor can reach and keep the converting material at 350 °C at a pressure of 220 bar for a residence time of 5 to 24 min. The solid content can be filtered in-line or separated at the end of the process depending on the physical characteristics of the suspended solid residues. Two different depressurizing system have been designed and implemented in parallel for the continuous discharge of the liquid products, widening the operability of the system to a larger selection of feedstock. The plant commissioning allowed to assess the process analysis in term of heating, pressurizing and reaction control. Flow rate, temperature and pressure profiles along the reaction and cooling zones have been acquired by a National Instrument data acquisition system. The software for data acquisition and for the control of the heaters and the depressurizing system was internally developed with NI LabView©.

1. Introduction

Hydrothermal liquefaction (HTL) is a thermochemical conversion process carried out in an aqueous medium, aimed to produce biocrude through the conversion of the organic structures of complex biomaterials. Generally, the process is performed in subcritical water, i.e. moderate temperature (250-370 °C) and high pressure (100-300 bar), but examples of HTL carried out at supercritical water condition do exist (Jensen et al. 2017). The reaction residence time is typically lower than 1 hour. The temperature is needed to initiate pyrolytic mechanisms in the biopolymers, while the pressure has a secondary importance, as its main task is to keep water in liquid state and tune water properties (Elliott et al. 2015). This technology is rapidly gaining attention for its ability to treat wet biomass streams like algae, sewage sludge, and lignin from biorefineries (Miliotti et al. 2019) or paper mills (Ong et al. 2018). Most of the experiments published in scientific literature refers to batch experiments performed in autoclaves or small tubular reactors heated by hot sand bath. However, these studies suffer from the inherent limitations caused by the small and batch-wise adopted experimental setup. On the contrary, continuous units would lead to more reliable results, as, for example, the separation of reaction products could be carried out gravimetrically, i.e. without the aid of solvents (Castello, Pedersen, and Rosendahl 2018).
The continuous pilot HTL unit which is described in the present study was designed and built within the EU H2020 Heat to Fuel project (grant agreement number: 764675), following batch experiments performed with lignin-rich residue from lignocellulosic ethanol in a custom made test bench (Miliotti et al. 2019).

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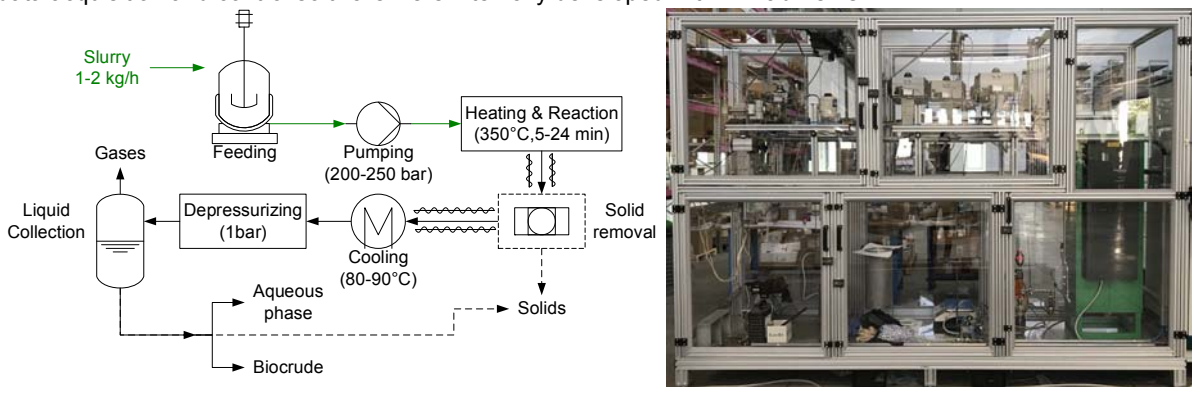
2. Plant description

Figure 1 shows a simplified sheme of the continuous unit. Feedstock pretreatment is not included, but generally, it consists in milling and in mixing with a specific amount of water and, if needed, with a certain quantity of homogeneous catalyst. The prepared slurry, contained into a stirred tank, is pumped to the working pressure by a high-pressure pump and reaches the reaction temperature directly in an electrically heated plug flow reactor. A water-cooled heat exchanger decreases the products stream's temperature in order to quench any undesirable reaction that could reduce the biocrude yield. The temperature of the stream should not be lowered to ambient temperature because of biocrude's expected increase in viscosity that would compromise the stream's flowability. On the other hand, the after-cooler temperature should not exceed 100 °C to avoid water evaporation once the depressurization to atmospheric pressure is accomplished. In order to keep the fluid at reaction temperature between the reactor and the cooler, heat tapes were wrapped around tubes, valves and filters; similarly, heat tapes set at 80 °C were adopted between the cooler and the depressurization system. Two alternative pressure letdown systems have been implemented: the first consists in a 1:1 dome-loaded backpressure regulating (BPR) valve, while the second is composed by two oleodynamic pistons. When the former system is used, a prior hot pressurized filtration system is adopted in order to avoid clogging of the small passages of the BPR valve; whereas in the latter case, the solid removal step could be bypassed. The solid removal system is composed by two parallel inline filters (up to 100 µm), whose flow in the respective lines is switched by four ball valves, accordingly to the filter pressure drops. Liquid and gas products are finally collected at ambient pressure in a tank, where the no condensable gases are vented. The data acquisition and control software were internally developed with NI LabView©.



a) b)

Figure 1: Simplified flow chart (a) and picture of the HTL pilot plant (b, insulation and piston system not shown).

3. Design

3.1 Selection of operating parameters

The continuous HTL unit has a lab-scale capacity (1-2 l/h of processed slurry), which was defined by the project, so to have the highest flexibility in terms of plant operability. Reaction temperature, residence time and biomass loading were defined after a batch experimental campaign, consisting in 350 °C, 5-24 min and 10 wt.% biomass-to-liquid mass ratio. Reaction pressure was autogenous in the batch experiments, here its value was defined by the design process.

Because of the very harsh process conditions, various challenges arose during the selection of the components: the processed fluid is mildly corrosive and therefore the use of stainless steel is needed, the high operation pressure in conjunction with moderately high temperature entails components with special material (especially for gaskets) and high pressure pumps capable of process solid suspensions are needed. As the size of the plant decreases towards small units these problems worsen. In addition, small plants are characterized by very low flow rates and therefore blockage of pipes and valves, due to the settling of the slurry solid particles, can easily occur. For these reasons, the selection of suitable components has been one of the most difficult and time-consuming tasks.

Due to the nature of the HTL process, in the reaction zone of the plant the components are subjected to high pressure and moderately high temperature conditions. The whole system can be considered as a heated pressure vessel and needs to be designed following existing guidelines for pressurized equipment. Moreover, the plant must comply with the current EU regulations for pressurized assemblies, such as the Pressure Equipment Directive (PED) 2014/68/EU (European Parliament 2014). Due to the parts volumes and pressure, the PED category indicated was the SEP (sound engineering practice), meaning that there are no specific

regulatory requirements for the design or production. Regarding the design of the pilot plant, the worldwide recognized guidelines included in the ASME Boiler and Pressure Vessel Code (BPVC) Section VIII Division 1 (American Society of Mechanical Engineering 2013) were followed. The pressure-temperature ratings of the selected components were verified in accordance with material strength limits listed in 2015 ASME Boiler and Pressure Vessel Code, Section II – Materials (American Society of Mechanical Engineering 2015). The valves were verified in accordance to the classes limit proposed in the ASME B16.34 (American Society of Mechanical Engineering 2004). In accordance with the ASME BPVC Section VIII, the two main parameters to be considered are the maximum allowable working pressure (MAWP) and the maximum allowable working temperature (MAWT). The weakest components were chosen as design point for the maximum operating conditions. The pressure system design followed a sequential iterative path: first a nominal working pressure had been chosen, then a pressure fluctuation had been considered to obtain the peak pressure (maximum working pressure), in the end the MAWP was calculated as 110% of the maximum working pressure. An appropriate temperature de-rating coefficient has been considered for the tubing (0.82, as given by the manufacturer for AISI 316 stainless steel) and the maximum pressure has been decreased from the nominal 517 bar. Table 1: Design specification.Table 1 reports the design specifications.

Table 1: Design specification.

Parameter	ID	Value	Unity of measure
Working Temperature	WT	350	°C
Max Allowed Working Temperature	MAWT	370	°C
Design Temperature	DT	370	°C
Nominal Pressure	NP	218	bar
Pressure fluctuations after damper	2%NP	4.36	bar
Min Working Pressure	WP-min	214	bar
Max Working Pressure	WP-max	222	bar
Max Allowable Working Pressure	MAWP	249	bar
Design Pressure	DP	249	bar
Operating margin	OM	14	bar

3.2 Pump selection

The pressurization step represents a critical phase in the whole hydrothermal process because of the handling of solids at high pressure. In general, the use of volumetric pumps is preferred over centrifugal pumps, because the performance of the latter is more sensitive to solid loading. Piston pumps are among the best candidates for HTL application as they are highly reliable in feeding viscous material. Rotary lobe pumps can process slurry with fibrous particles at high temperatures without the need of using check valves, which are the components that are most sensitive to plugging; however, they can't attain high hydraulic head and several pumps must be connected in series in order to reach the required pressure (Berglin, Enderlin, and Schmidt 2012). In the present plant a single piston pump (Sigma/ 2, Prominent) was installed. The selected pump has a capacity between 1 and 2 l/h and can reach up to 320 bar.

3.3 Reactor and cooler design

Firstly, a plug flow reactor with recycle was investigated, as adopted in the CatLiq process (Hammerschmidt et al. 2011). The advantage of the recycle consists in an increase in the flow velocity inside the reactor and, consequently, plugging risk is reduced. Furthermore, greater diameters can be adopted, making the adoption of heterogeneous catalyst a viable option. However, no commercial pump able to withstand HTL conditions was found. Eventually, a modular plug flow reactor without recycle was designed; the lack of the recycle allows a clear evaluation of the slurry residence time, which can be adjusted by regulating the feed pump's flow rate and/or by modifying the reactor's modules. The final reactor configuration consisted in five sections of ¼" tube coils (total length 30 m) inserted in an electrically heated oven (400x400x1200 mm; maximum power 4.5 kW). The reactor length was determined by considering the heat required to bring the fluid from ambient temperature to the MAWT. Because of the very low flowrate, the flow regime resulted laminar and consequently the Nusselt number was assumed 4.36, under the hypothesis of constant and stable heat flow. The oven was designed considering the total heat dispersion to the ambient. The air inside the oven was considered at a constant temperature of 400 °C like the case walls' inner surface. The heat released to the ambient was evaluated separately for the oven case's side, top and bottom walls, because different correlations have to be used to determine the Nusselt number; however, the procedure is the same for the three cases: the heat exchanged across metal and insulating walls was equaled to the heat released by external natural convection. Because the insulating panel's outer surface temperature was unknown, an

iterative calculation was done. The conductive heat through the metal and insulating walls and the outer natural convective heat are given by:

$$\dot{Q}_{cond} = \frac{A\left(T_{wall,in} - T_{wall,out}\right)}{R_{metal} + R_{ins}} = \dot{Q}_{conv,out} = h_{conv,out} A\left(T_{wall,out} - T_{amb}\right) \quad \text{Eq. 1}$$

Where R_{metal} and R_{ins} are, respectively, the thermal conductive resistances of the case side walls and of the insulating panel; they are both defined as their thickness to conductivity ratio. The heat transfer coefficient $h_{conv,out}$ is evaluated with the Nusselt number, that is defined by the following correlations (Çengel 2009) for side, top and bottom walls (Ra and Pr are the Rayleigh and the Prandtl numbers):

$$Nu = \left\{0.825 \frac{0.378 Ra^{1/6}}{[1 + (0.492/Pr)^{9/16}]^{8/27}}\right\}^2 \qquad Nu = 0.15 Ra^{1/3} \qquad Nu = 0.27 Ra^{1/3} \quad \text{Eq. 2}$$

The total heat which must be provided by the oven resulted in ~2 kW, however a nominal electric power of 4.5 kW was selected in order to investigate the effect of higher reaction temperatures.
The cooling of the reaction stream was accomplished by adopting a water-cooled tube-in-tube heat exchanger obtained from a combination of bored-through tee fittings and ¾" outer tube. The inner tube, in which the reacted stream flows, is a ¼" tube. Similar iterative calculations were adopted for the evaluation of heat exchange area and temperatures, by adopting the ΔT_{ml} method.

3.4 Pressure letdown system

The first depressurization system which was selected was a special BPR valve (Equilibar, USA), which is equipped with a flexible diaphragm subjected to the balance of three separate pressures: the fluid inlet and outlet pressure and the pilot set-point pressure, that is applied on its non-wetted side. The valve operates in a 1:1 ratio, so a 300 bar Ar cylinder was used for the regulation of the pilot pressure. Because of the multiple orifices that are present in the membrane, the valve leads to a constant performance with a very wide range of flow rates, but can't be operated with suspended solids and, therefore, a prior filtering must be carried out.
The alternative pressure letdown system consists in the use of two hydraulic pistons designed to work at a nominal pressure of 250 bar. These top pistons are mechanically connected to an external oleodynamic circuit. As the process pistons volume is overdesigned (0.5 l each), a small fraction of solids in the fluid can be accepted and therefore the filtering step can be avoided.

3.5 Safety equipment

Due to the required elevated pressure, it is of the utmost importance to define appropriate safety equipment. The unit is equipped with four redundant "safety systems", each one consisting in a capacitive pressure transducer (Trafag), a high-pressure relief valve (HPRV) and a rupture disk (RD). These systems are placed before plant's critical points, where tube plugging is foreseen to be more possible, and have the task of avoiding pressure buildups. A first intervention is done by the logic of the control system, reading the value of pressure acquired by the sensor; if the control system fails to reduce plant pressure the HPRV, which is a spring-loaded valve set to open above the MAWP, will relief the plant pressure. In the worst-case scenario of both control logic and HPRV failing, the RD will burst, ensuring a sudden decrease in the system pressure.
The HPRVs that were selected considering a flow passage area greater than the one required in the following worst-case scenario: all oven thermal power absorbed by the fluid, whose state is completely changed into vapor, leading to a chocked flow. The equations for the calculations were obtained by the guidelines provided by the American Institute of Chemical Engineers (Crowl and Tipler 2013). The area in the worst-case scenario was 0.38 mm^2, therefore, a standard HPRV with ¼" connections was chosen as it provided a flow passage area of 10.2 mm^2. Given that ¼" tube provides suitable passage area, a bigger ½" size of RDs and discharge line was chosen in order to keep the flow velocity to low levels.

4. Commissioning of the pressure letdown system

This paragraph reports the results of the testing of the two pressure letdown systems, i.e. the BPR valve and the piston system. Both tests were carried out by using demineralized water. The heaters were not activated during these tests.

4.1 Backpressure regulating valve

The aim of the test was to verify the pressure oscillation of the BPR and to identify leakages in the plant. The system pressure was set by adjusting the BPR pilot pressure to 50 and then 100 bar. The piston pump flowrate was set to 1.9 l/h. Average pressure was 102.6 bar, while oscillations are kept within +3 and -1.2 bar.

In order to identify possible leakages in the fittings and evaluate the sealing action of the ball valves, both filters lines were isolated, and the flow in the plant was maintained through a bypass line. In this latter test pressure was set to ≈ 50 bar. When filter lines were isolated by closing the ball valves, the line pressures (P4 and P5) started to gradually decrease due to a small leakages in the filters fittings, as reported in Figure 2 and consequently lines maintenance were carried out by tightening the relative fittings.

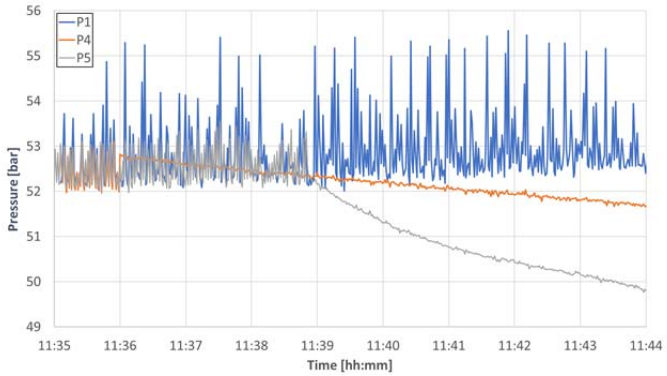


Figure 2: Pressure values showing leakage in the filter's lines during the BRR testing.

4.2 Piston system

The aim of the test was to verify the functioning of the two pistons: while one piston is being filled, the other is discharging into the outlet tank; as the pistons have only one connection to the process, four pneumatically actuated ball valves were installed for correct operation (two at the inlet and two at the outlet of each piston). In the test the flow was delivered by the pump through the bypass line and the pressure was set to 200 bar. Set pressure was easily reached and maintained until the first piston was filled; when the switch to the other piston occurred, the plant was completely depressurized, as for few seconds the inlet and the outlet valves of the pressure let-down system were both open, connecting the plant to ambient pressure. A new sequence for the opening and closing of the valves was implemented in the control software. However, the problem was only partially solved as a decrease of nearly 70 bar was detected during the switch (Figure 3a). This decrease was due to the fluid expansion in the empty piston after its discharge. This pressure reduction should be absolutely avoided as it can lead to water evaporation if the system when pressure goes below saturation level. To eventually solve the problem, the closure of the outlet valve of the discharging piston was anticipated. In this way, the complete depressurization of the piston volume was avoided, and the pressure decrease after the switch eliminated. However, as reported in Figure 3b, a sudden increase in pressure is detected after each piston switch. This behavior was due to the control of the oleodynamic circuit and was solved by implementing a PID algorithm for the opening of the oil proportional valve (Figure 3c). In this latter configuration, the pressure variations were kept below ± 2 bar (during piston filling) and + 6 bar after the switch.

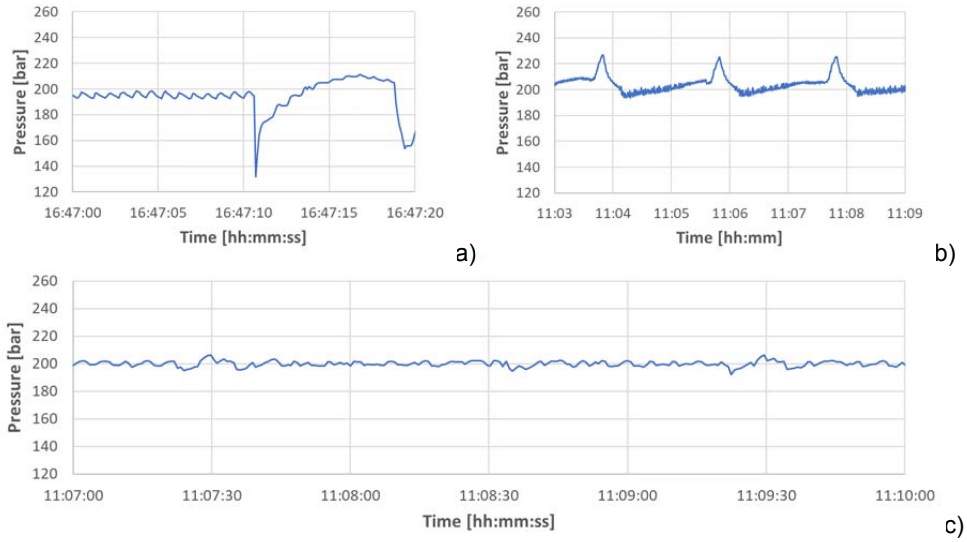


Figure 3: Pressure decrease during piston switch (a); pressure increase after anticipated closure of inlet valve (b) (the switch is occurring every two minutes); pressure fluctuation after PID implementation (c).

5. Conclusions

A continuous hydrothermal liquefaction unit of 1-2 l/h capacity was designed and built. The whole process design was carried out after a batch experimental campaign, screening several operative points by varying temperature, time and solid load. The pressure equipment selection and design followed ASME guidelines as well as the implementation of safety redundant systems.
Pressure tests were carried out on the system observing the behavior of the two installed pressure letdown systems and troubleshooting. No problems were encountered with the BPR valve, whose performance was good, limiting pressure oscillation to + 2.9% and -1.2% with respect to the average pressure (102.6 bar). The matching between the high-pressure pump and the piston system was more challenging as the correct sequence of opening and closing of four ball valves was involved in the operation. Pressure spikes due to the oleodynamic control circuit were eliminated thanks to the implementation of a PID algorithm. Eventually, pressure variations were under ± 2% during the filling of the piston and below + 3% after the piston switch (set pressure 200 bar).

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