

# Effect of Heating Rate on the Performances of HTL Applied to a Sewage Sludge

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The use of renewable energies and the energy exploitation of residual biomass have become prominent topics in the context of sustainable development goals. From a circular economy perspective, among the different types of biomasses, those defined as “waste” such as sewage sludge are of particular interest since significant volumes of municipal/industrial sludge are discharged into landfills at great cost to the industry and with associated negative environmental impacts. In this context, the hydrothermal liquefaction (HTL) process, working with water in sub-critical conditions, appears to be a promising and still limitedly explored route (as compared with other thermochemical processes) to obtain biofuel from biomass characterised by a high moisture content such as sludge. However, most of the literature studies are based on HTL experiments performed in small-scale batch reactors (generally a few mL), not allowing for proper assessing the effect of thermal transients, which instead occur in larger-scale systems, on product yields and quality.

In this work, the set-up of a 500 mL lab-scale HTL apparatus was optimized so as to limit the duration of thermal transients, and preliminary tests were carried out on a municipal sludge to evaluate the yield and quality of the bio-crude obtained at different heating rates.

## 1. Introduction

The use of renewable energies and the exploitation of biomass for the production of energy carriers have become important issues in the context of sustainable development. The efficient use of biomass as a widely available and flexible fuel source represents a potential option to face the ever-increasing energy demand (Balsamo et al. 2023), in particular for developing countries which experience significant population growth and usually lack the proper infrastructure to import fossil fuels. Biomass can be converted into several useful forms of energy employing different valorization treatments that are essentially divided into chemical (Han et al. 2020), biochemical (Náthia-Neves et al. 2018), and thermochemical (Sharma et al. 2014; Zhou et al. 2021; Fan et al. 2022). Among several available biomasses in recent years there is an increasing interest in the energetic valorization of waste substrates whose disposal involves remarkable costs for the producer, such as sewage sludge (Lee et al. 2019).

In this work, the energetic valorization of a municipal sludge was evaluated via the innovative hydrothermal liquefaction (HTL) process, where the target product is bio-oil, also termed bio-crude (Toor et al. 2011; Vardon et al. 2011; Fan et al. 2022). HTL is an emerging technique for the conversion of wet biomass into biofuels by processing it in a hot and pressurized water (200–350 °C and 15–220 bar) to break down the solid biopolymeric structure and produce a bio-oil as energy vector (Kumar et al. 2018; Wang et al. 2018). The main advantage of the HTL process is that it does not require preliminary procedures for drying the raw material which are highly energy-intensive, as water under process conditions acts as a catalyst and reaction medium. The HTL process promotes the depolymerization of bio-macromolecules by hydrolysis, followed by reactions of dehydration,

decarboxylation and deamination. Finally, the reactive fragments and free radicals thus generated (phenols, organic acids, furfural, etc.) are recombined by polymerization, condensation, and cyclization reactions leading to the formation of a wide range of organic compounds with reduced molecular weight (Dimitriadis and Bezergianni 2017; Gollakota et al. 2018). The target product is a bio-crude with a reduced content of heteroatoms (essentially, N and O) with respect to the starting biomass. Other co-products include: i) an aqueous phase, rich in water-soluble organic products such as alcohols, acids, phenols, ketones and nitrogen species (Watson et al. 2020); ii) a gas phase rich in CO<sub>2</sub> and also containing CH<sub>4</sub> and H<sub>2</sub> as minor components (Basar et al. 2021); iii) a solid residue (bio-char), potentially exploitable, e.g., as an adsorbent in purification operations (Saner et al. 2022). For the recovery of bio-crude from the other phases produced after the HTL test, the use of extraction solvents is widely reported in the literature and, among the different solvents, dichloromethane (DCM) has a very good bio-oil extracting capacity (Jahromi et al. 2022).

HTL is mainly investigated in batch reactors, and several studies have shown that a high heating rate positively affects the yield in bio-crude. So, during the HTL process in a batch reactor, the minimization of the duration of thermal transients is crucial to obtain a high-yield bio-crude with more attractive energy properties (Qian et al. 2020; Ni et al. 2022).

Most of the literature is based on studies of small-scale HTL batch reactors (10–100 mL) and, consequently, the effect of thermal transients on product yields is poorly investigated. In this study, starting from a previous work of this research group (Di Lauro et al. 2022), the set-up of a lab-scale plant consisting of a 500 mL batch autoclave was performed and optimized for the execution of HTL tests under controlled temperature and pressure conditions. The selection of proper insulation and heating systems was made to minimize thermal transients that could lead to the formation of undesirable products, and negatively affect the proper evaluation of the time-dependent evolution of phases produced along the isothermal stage of the HTL process. Then, municipal sludge was subjected to the HTL process to study the effect of different reactor configurations (different heating ramps) on the distribution of products and, in particular, on the bio-crude yield.

## 2. Experimental

### 2.1 Lab-scale apparatus for HTL tests

HTL tests were carried out in a 500 mL nickel-chromium-molybdenum alloy (Hastelloy C-276) reactor, detailed in Di Lauro et al. (2022). In this work, to limit the formation of undesirable products along the HTL process, the lab-scale reactor was furtherly upgraded; in particular, the heating stage was carried out both with the electric heater present around the reactor and with the support of a band heater (Watlow Series MI band) with a power of 1250 W, coupled with a cylindrical steel block located on the bottom of the vessel. Three configurations were compared in terms of heating/cooling rate:

- Configuration A: corresponding to the reactor as received;
- Configuration B: where the heating stage was carried out also with the support of a 1000 W heating plate of 145 mm diameter, located on the bottom of the vessel, and the top of the reactor was insulated with a layer of rock wool;
- Configuration C: where, with respect to B configuration, a band heater of 114.3 mm internal diameter and 63.5 mm height (Watlow Series MI band), with a power of 1250 W, was implemented and coupled with a cylindrical steel block located between the reactor and the heating plate. Temperature control of this system is guaranteed by coupling the heating band with a PID controller, series PXU21A20.

For the heating/cooling test, the reactor was loaded with 300 mL of distilled water and pressurised at 30 bar with nitrogen. Then, it was heated to the temperature of  $T=350$  °C, and the evolution of temperature and pressure was monitored over time. To study the effect of reactor configuration on the yield of bio-crude, the reactor was loaded with 30 g (dry basis) of municipal sludge together with 270 mL of distilled water, so as to obtain a slurry with a 10%wt solid content. Then, the reactor was purged four times with nitrogen at 5 bar to remove the oxygen present in the vessel, and then pressurised at 30 bar. Subsequently, the system was heated at 300 or 350 °C to reach the desired pressure of 200 bar and kept at the desired  $T$  level for 20 min (isothermal stage). After the HTL tests, the reactor was quickly cooled to “freeze” chemical reactions, thus minimizing product re-distribution during thermal transients. Finally, the reactor is depressurized, and the reaction products recovered with about 30 g of DCM.

### 2.2 Sewage sludge characterization

The municipal sludge used in this work was described by Di Lauro et al. (2022). The main properties of sludge are total C content of 34.6% and higher heating value (HHV)=16.7 MJ/kg. These values are in line with data commonly reported for sludge (Jiang et al. 2010, Dong et al. 2015). Prior to the HTL test, the biomass was dried in an oven at 105 °C, until no change in weight was observed.

## 2.3 Products separation protocol

The separation protocol already described in Di Lauro et al. (2022) was further optimized so to improve the recovery of products and reduce the use of the extracting solvent (Figure 1). The procedure used in this work involves a solid recovery by Büchner vacuum filtration and washing with DCM. The solid is then subjected to Soxhlet extraction with 150 g of DCM for the recovery of bio-oil from the pores of the solid residue, while the liquid phase is subjected to centrifugation in a NEYA 8 BASIC ventilated apparatus. Centrifugation was performed for 10 min at 4000 rpm, obtaining the stratification between the aqueous and the oily phase which is then recovered with Pasteur pipettes. At the end of these operations, the solid residue was oven-dried at 105 °C for 24 h, and the bio-crude (recovered from both Soxhlet extraction and centrifugation) was subjected to vacuum distillation at 0.4 bar for DCM evaporation.

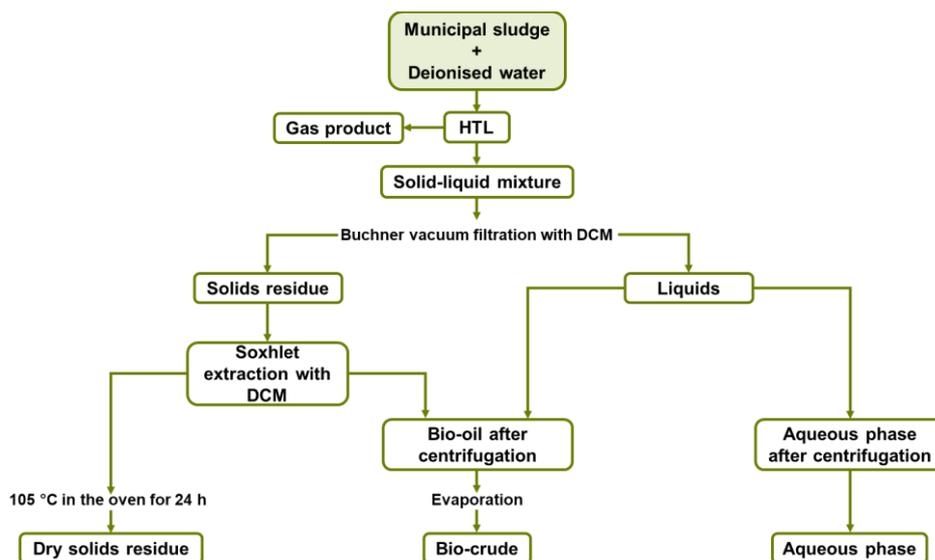


Figure 1: Experimental protocol for the separation of HTL products.

## 3. Results

### 3.1 Comparison of reactor configurations

Blank tests were carried out to determine the system response during the heating and cooling stages by varying the reactor configuration. The overall objective was to maximize the heating rate to limit the formation of undesirable products along the HTL process.

Figure 2 shows the time trend of the reactor temperature for the different configurations investigated when 300 mL of distilled water were heated at a set point  $T$  of 350 °C. It can be observed that in configurations A (absence of insulation and auxiliary heating systems), B (presence of insulation and heating with plate at the base of the reactor) and C (addition of a band heater compared to configuration B), the system requires, respectively, 90, 55 and 48 min to reach  $T=350$  °C. For all three systems, the cooling stage is very fast and in the order of 5–7 min, thus achieving a “quench” to avoid the occurrence of secondary reactions that could lead to a redistribution of products during the cooling phase.

Then, to complete the set-up phase of the experimental apparatus, the influence that the presence of sludge could have on the  $T$ - $P$  couple during a typical HTL test was investigated, compared to the non-reactive case. Figure 3 shows the  $T$ - $P$  pattern for an HTL test conducted at 350 °C for 20 min in configuration C, which is overlapping on the blank curve (distilled water only). It is observed that the sludge does not significantly influence the temperature-pressure curve due to its low concentration in the reactive system (about 10% by weight), hence, it affects to a negligible extent the thermal properties of the aqueous phase. Only at the final  $T$ ,  $P$  is slightly higher than in the blank test, which is due to gas generation during HTL of the sludge (e.g., by decarboxylation reactions with  $\text{CO}_2$  generation).

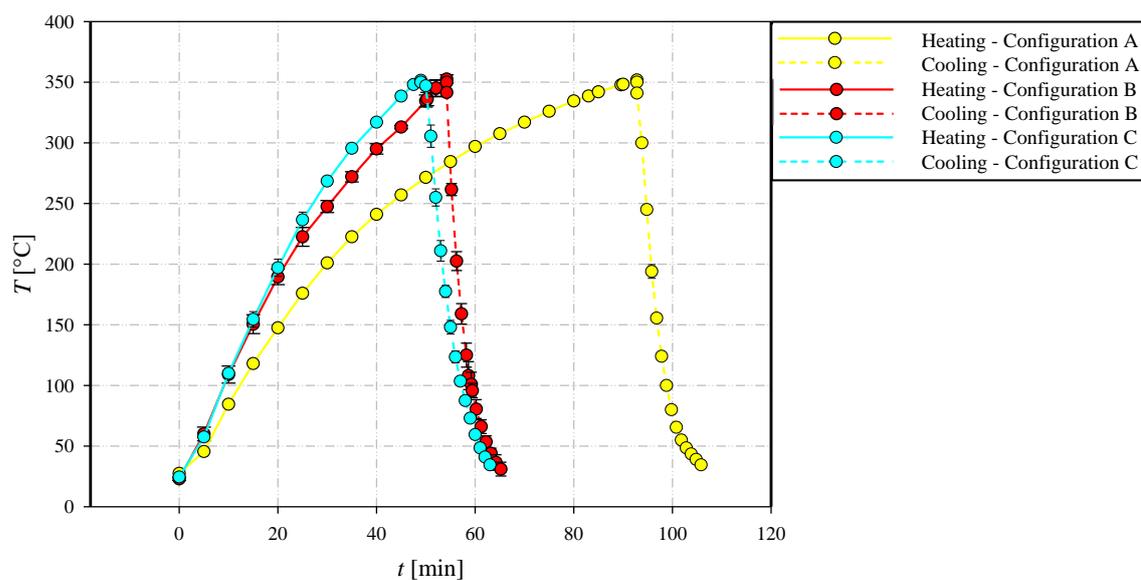


Figure 2: Set-up of the purposely designed batch autoclave reactor for HTL. Results of the heating/cooling test for configurations A, B and C, using distilled water.

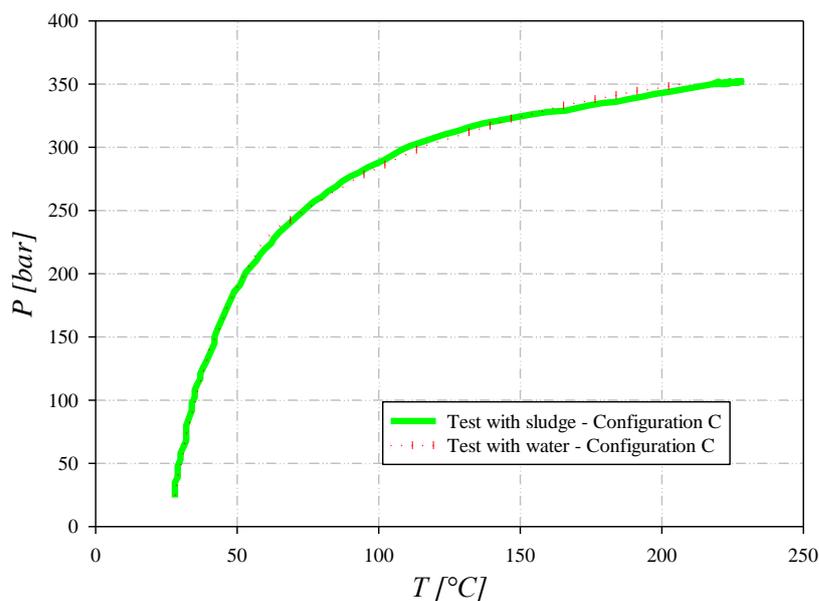


Figure 3: Comparison of temperature vs. pressure profile between blank test and sludge test, configuration C.

### 3.2 Effect of reactor configuration on product distribution

HTL tests at different reactor configurations were performed to assess their effect on the bio-oil and co-product yields. In this study, configuration A was discarded due to the observed unfavourable longer heating times. Figure 4 shows the yields of the bio-crude, solid and gaseous phases produced with a different heating ramp at temperatures of 300 and 350 °C and for an isothermal stage of 20 min. It is possible to observe that, at fixed  $T$ , there are no relevant variations in the gas and solid yields when the heating rate changes. On the other hand, when bio-oil is considered, for the tests carried out at 300 °C (B-300-20 vs. C-300-20), an increase of  $Y_{bio-crude}$  of 2% is observed for configuration C with respect to the B case; on the contrary, for the tests carried out at  $T$  of 350 °C, a decrease in the bio-crude yield for configuration C of about 10% can be noted (it is about 45% for

configuration B). However, it is important to note that, when operating at peak temperature of 350 °C in configuration B, the reaction time in the non-isothermal stage is longer than for configuration C, the overall reaction time being longer by about 8 min as compared with that experienced by the sludge processed to the same maximum temperature in configuration C. Moreover, the comparison of the heating values of bio-oils obtained in the tests at 350 °C and 20 minutes for the two configurations indicates that HHV is 31.4 MJ/kg for operation in configuration C, 3.7% larger than the HHV of bio-oil obtained from configuration B (Table 1).

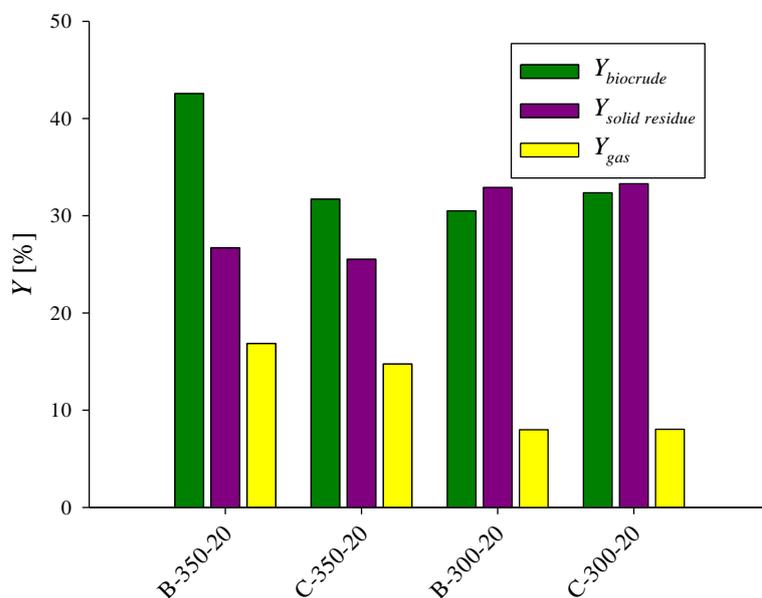


Figure 4: Yields ( $Y$ ) of bio-crude, solid and gas phase for HTL tests performed for configurations B and C (temperatures of 300 and 350 °C, isothermal stage of 20 min). Yields of bio-crude and gas are expressed with reference to the initial mass of sludge on *dafb* (dry and ash-free basis), while the yield of solid residue is expressed with reference to the initial mass of sludge on *db* (dry basis).

Table 1: Higher heating value of bio-crude obtained for different heating rates.

Test	HHV [MJ/kg]
B-350-20	30.33
C-350-20	31.44

#### 4. Conclusions

Hydrothermal liquefaction of municipal sludge was investigated in a 500 mL reactor operated batchwise. The study focused on the optimization of the reactor configuration and on the effect of different heating rates on the yield and quality of bio-crude, the target product of the process. Results show that the improved design of the heating system, brings about the production of bio-oils of better quality compared to the base-case design. In particular, increasing the heating rate to about 8 °C/min positively affects the quality of bio-crude: HHV of bio-oli is 31.44 MJ/kg at maximum process temperature of 350°C at the highest heating rate, nearly 4% larger than HHV of bio-oil obtained with slower heating.

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