

Waste Reduction and Bioenergy Generation from Secondary Sludge using Hydrothermal Liquefaction

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Given its global accessibility and high organic content, biogenic waste such as sewage sludge currently represents a valuable renewable resource for energy production. Hydrothermal liquefaction (HTL) stands out as one of the most suitable technologies to convert these feedstocks into biocrude, a valuable biofuel precursor. This process operates at moderate temperatures and high pressure in the presence of water, eliminating the need for energy-intensive preliminary dewatering steps when treating high-moisture feedstocks. This study focuses on investigating the effects of various reaction temperatures and holding times on biocrude yield and quality obtained from batch HTL conversion of digested secondary sludge derived from paper mill facilities. Experiments were conducted at temperatures of 280, 300 and 330 °C, with holding times ranging from 0 to 35 minutes. Optimal conditions were identified at 300 °C and holding times between 10 and 35 minutes, resulting in biocrude yields of 20-21%, higher heating values (HHV) of 35 MJ kg⁻¹ and energy recovery of 54-59%. The findings underscore the potential application of HTL in waste biomass disposal cycles, contributing to waste minimisation and enhancing the bioenergy recovery.

1. Introduction

The current global interest in a sustainable path for humanity's development has led to an ever-growing demand for sustainable energy sources and waste-minimization solutions. Exploring the potential of generating energy from municipal and industrial biogenic wastes offers a promising avenue to both minimize and energetically valorise such wastes, enhancing the efficiency of production cycles. Sewage sludge derived from municipal and industrial wastewater treatment emerges as a compelling feedstock for bioenergy production due to its high organic content and widespread availability. The production of sludge is even high enough to generate challenges related to its management. For instance, European Union estimates from 2003-2007 indicated an annual generation of over 10 million metric tons of dry sludge (Kelessidis, Stasinakis, 2012), creating significant management issues. Common disposal strategies involve utilizing sewage sludge as nutrient source for crops, encompassing landfilling, composting, nutrients recovery for fertilizer production, as well as energy extraction through anaerobic digestion, incineration and thermochemical processes for biofuel production (Fan et al., 2022). Its high content of organic substrates, nitrogen and phosphorous, makes sewage sludge a low cost fertilizer that can be added to the soil to enrich its concentration in bioavailable nutrients for crops, directly or after being composted. However, this use can be strongly limited depending on sludge's origins, as it may contain toxic organic compounds and heavy metals that can be accumulated in the soil and even persist in the food chain (Delibacak et al., 2020). Furthermore, the high moisture content of sewage sludge, that is linked to its origin from wastewater treatments and typically exceeds 90% (Cabrera, Labatut, 2021) is an obstacle for incineration process, as it negatively affects the heating value of the feed, and for thermochemical processes as gasification and pyrolysis, for which a dry feedstock is required to achieve an overall positive energy balance (de Caprariis et al., 2017). In this context, hydrothermal liquefaction (HTL) emerges as a promising technology that offers several advantages for the conversion of high moisture biomass into valuable biofuels. Subcritical HTL is a thermochemical process that works at high pressures (7-20 MPa) and medium temperatures (250-350 °C) in the presence of water.

In these conditions water is near its critical state and behaves as a slightly polar solvent and acid/base catalyst, as its dielectric constant decreases and its ionic dissociation product increases (de Caprariis et al., 2022). Several reactions occur on the organic substrate, including hydrolysis, depolymerization, further transformations and repolymerization, some of them competing with each other. The main product of the process is a biocrude, a heavy oil that can be upgraded to a liquid biofuel. Three other by-products are generated: a gaseous phase mainly composed by CO₂ that is usually not suitable for energy recovery, an aqueous phase rich in water-soluble compounds, and a biochar. The upgrading step of the biocrude is required, as it is chemically unstable and its content of oxygen and other heteroatoms as nitrogen and sulphur are over the limits for a liquid fuel. The required presence of water as reaction medium in HTL allows to avoid the need to remove water from the starting feedstock, an energy intensive step that can account for more than 75% of the total energy consumption of the process (Hao et al., 2021). These characteristics allow the HTL process to be integrated with other consolidated technologies for waste valorisation, as anaerobic digestion. The HTL of sewage sludge is a topic that received much attention in literature, although results may vary a lot with sludge's origins and with the scale of the experimental set-up (Fan et al., 2022). This variability hinders the search for optimal reaction conditions and suggests the need to develop flexible processes for the scale-up to industrial plants. The aim of this work is to study the effects of operating conditions, as temperature and reaction time, on the conversion of a digested secondary sludge to produce a liquid biofuel precursor, that can potentially be fed to conventional fuel upgrading processes to produce a high quality liquid biofuel. The optimal operating conditions, in terms of biocrude yield and energy recovery from the sludge, are investigated using an experimental setup that allows a fast heating of the feedstock, as achieving a high heating rate is crucial for the scale up to a continuous process.

2. Experimental section

2.1 Materials

Pre-dried digested secondary sludge derived from papermill facilities was provided by a wastewater treatment company in Italy. Dichloromethane (>99.8%) was purchased from J.T.Baker and was used as solvent for biocrude extraction.

2.2 HTL reaction set-up

HTL batch reactions were carried out using tubular stainless-steel autoclaves with an internal diameter of 10 mL filled with 1 g of dry feedstock and 5 g of deionized water (water to dry ratio 5:1). The autoclaves are closed, inserted in a pre-heated sand bath and mixed continuously with mechanical stirrer. The pressure inside the autoclave is generated by the vapor-liquid equilibrium of water (reaching pressures of 65-130 bar depending on the set point temperature) and the temperature is fixed by the sand-bath temperature. This set-up allows to reach heating rates up to 100 °C/min.

Three different temperatures were investigated:

- 280 °C
- 300 °C
- 330 °C

Autoclave's temperature was continuously measured connecting a thermocouple to the autoclave's external wall, with the thermocouple extremity thermally insulated from the sand. This measurement started from room temperature and took approximately 3 minutes to reach the selected final temperature for each test. After that, the holding time under isothermal conditions was measured. For each reaction temperature, the investigated isothermal holding times were:

- 0 min
- 10 min
- 20 min
- 35 min

For better understanding the trend of the product yields, some additional tests were carried out at different holding times. Then, the autoclave was removed from the sand bath and quenched in cold water to immediately freeze the ongoing reactions.

2.3 Separation and evaluation of the yields of the products

After the quenching, the autoclave is dried and weighted in order to exclude any losses. Then it's opened and left for 15 minutes to release the gaseous phase and weighted again. The gaseous phase is evaluated by difference. The aqueous phase is removed by filtration using a filtering cap equipped with a piece of filter paper (20 µm of pore diameter) that is directly mounted on an extremity of the autoclave.

A known amount of aqueous phase is poured on a watch glass and let evaporate at room temperature for 24 h. The residue of the evaporation is weighted and used to evaluate the soluble organic fraction in the aqueous phase.

The filtration residue is transferred in a Soxhlet cellulose thimble, while the autoclave is washed with dichloromethane to collect the oil stuck on the internal wall. The thimble is mounted in a Soxhlet extractor charged with 100 mL of dichloromethane. The extraction is carried out for 4 h. Dichloromethane is then evaporated under vacuum and the obtained biocrude weighted. The thimble is dried for 24 h at 80 °C in order to remove the solvent and then weighted to evaluate the biochar yield.

The dry based yields are calculated dividing the weight of the product by the weight of the initial dry feedstock.

2.4 Analysis of feedstock and products

The elemental analysis of the starting feedstock and the obtained biocrude was carried out using an Eurovector EA3000 elemental analyzer. The higher heating value (HHV) of the dry feedstock and its derived biocrudes at different conditions were calculated using the Dulong formula (Hongthong et al., 2020), reported in Eq(1):

$$\text{HHV} [\text{MJ kg}^{-1}] = 0.338 \cdot \text{C} + 1.428 \cdot (\text{H} - \text{O}/8) \quad (1)$$

C, H and O are respectively the dry based weight percentages of carbon, hydrogen and oxygen in the sample. The percentage of energy recovery (ER%) was calculated comparing the HHVs of the biocrudes and the dry feedstock, considering the dry based biocrude yield (Y_{biocrude}), as reported in Eq(2):

$$\text{ER}\% = \frac{Y_{\text{biocrude}} [\% \text{ d.b.}] \cdot \text{HHV}_{\text{biocrude}} [\text{MJ kg}^{-1}]}{\text{HHV}_{\text{dry feedstock}} [\text{MJ kg}^{-1}]} \quad (2)$$

3. Results and comments

3.1 Analysis of the feedstock

The elemental percentages, ash content and higher heating value of the dry secondary sludge used as feedstock for the tests are reported in Table 1.

Table 1: Elemental analysis, ash content and HHV of the dry feedstock

C [% d.b.]	H [% d.b.]	N [% d.b.]	Ash [% d.b.]	O* [% d.b.]	HHV [MJ kg ⁻¹]
31.5	4.9	5.3	29.2	29.1	12.45

* Oxygen obtained by difference: 100% – C – H – N – Ash.

The elemental analysis of the feedstock reveals a high presence of nitrogen (5.3%), due to the biologic origin of secondary sludge. Results also show an ash content of 29.2% and an oxygen content of 29.1% (calculated by difference), that both limit the heating value of the feedstock if directly used as fuel. The calculated HHV is 12.45 MJ kg⁻¹.

3.2 Product yields

In figure 1 the dry based yields of the measured biocrude, biochar, soluble organics and gaseous phase are reported as a function of time for the temperatures of 280, 300 and 330 °C.

The results of biocrude yields reported in Figure 1a show non-monotonic trends of biocrude yields for each temperature. The highest values of 20.99%, was obtained for the temperature of 300 °C and for the holding time of 35 min, followed by 18.59% for 330 °C and 20 min, and by 18.23% for 280 °C and 10 min. These values are consistent with other results reported in literature for the HTL of sewage sludge under similar conditions (Xu et al., 2018), although other studies report different values, higher than 30% (Cabrera and Labatut, 2021). This variability depends on origin and composition of sewage sludge and is one of the main obstacles for developing an optimized process. Results show that for short holding times the biocrude yield is lower at 330 °C respect to 280 and 300 °C. This disparity could be attributed to a higher production of light water-soluble organics at 330 °C. These compounds may not have sufficient time for further conversion and repolymerization to form biocrude. This may justify the higher losses during the evaluation of water-soluble organics in the aqueous phase, as part of the compounds with boiling points similar to water evaporates at room temperature and is not quantified.

After 10 min of holding time, the biocrude yield at 280 °C decreases and becomes lower respect to the yield at 330 °C, suggesting the occurrence of repolymerization mechanisms that are favored at lower temperatures and lead to the decrease of the yield in biocrude, increasing instead the yield in biochar.

Biochar yields are reported in Figure 1b and show slight variations in the range of 40-50% for all the operative conditions. The higher biochar yield of 49.45% is obtained at 280 °C and 0 min, although for that test both final temperatures and holding times may be too low for the complete conversion of the feedstock, with the result that unconverted solid may be present in the solid residue after biocrude extraction.

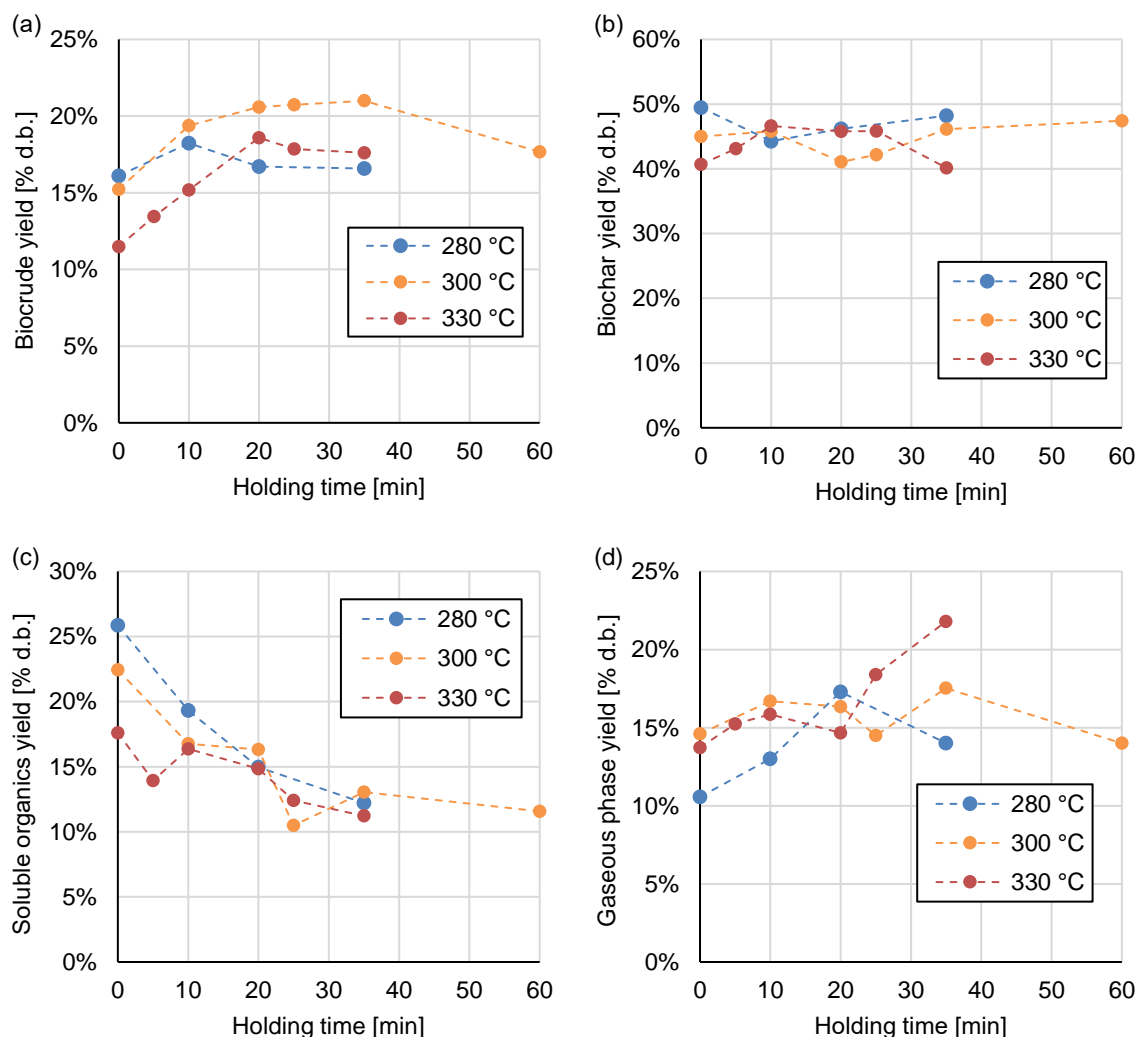


Figure 1. Dry based yields of the obtained HTL products as function of holding time for the temperatures of 280, 300 and 330 °C. (a), biocrude; (b), biochar; (c), water-soluble organics; (d), gaseous phase.

Figure 1c shows a general decrease of the yields in water-soluble organics in the aqueous phase with the increase of holding time, that appear to be lower for higher temperatures. The maximum yields of soluble organics are obtained for the holding time of 0 min, just after the heating ramp. Results suggest that these products are initially formed from depolymerization and hydrolysis of the substrate and then degraded to lighter compounds that enrich the gaseous phase, or converted to heavier compounds via repolymerization reactions, to enrich biocrude and biochar.

Figure 1d show an increase of gaseous phase yields after 20 min of holding time at 330 °C, while for lower temperatures there is no clear trend, and the yield may be affected by experimental errors due to water losses during the degassing step.

3.3 Elemental analysis of the product

The elemental percentages, HHV and ER% of the obtained biocrudes are reported in Table 2. All the biocrudes show similar results, with slight variations for carbon (66 – 74%), hydrogen (8.5 – 9.5%), nitrogen (6.5 – 8%) and oxygen (10 – 17%). The HHV is also similar for all the obtained biocrudes, varying from 31 to 36 MJ kg⁻¹. The results are consistent with literature both for elemental analysis (Ni et al., 2022) and HHV (Fan et al., 2022). Results show that higher temperatures lead to a higher carbon content and a lower oxygen content, while the percentages of hydrogen and nitrogen remain quite the same for 280 °C and 330 °C, and are both slightly higher for the temperature of 300 °C. The main effect of holding time, varying from 0 to 35 min, is the increase of the carbon content and the decrease of nitrogen and oxygen, as observed in Table 2. Combining the calculated HHV of biocrude and feedstock with the biocrude yields, it's possible to evaluate the bioenergy recovery (ER%) from the starting feedstock, that vary from the minimum of 30% for 330 °C and 0 min, to the maximum of 59% for 300 °C and 35 min. From the obtained data, it appears that the optimal conditions for energetic recovery are a temperature of 300 °C and holding time of 10 min or higher.

Table 2: Elemental analysis, HHV and ER% of the obtained biocrudes

Temperature [°C]	Time [min]	C [% d.b.]	H [% d.b.]	N [% d.b.]	O* [% d.b.]	HHV [MJ kg ⁻¹]	ER%
280	0	66.62	8.49	6.93	17.96	31.43	40.67
	10	68.77	8.54	6.63	16.05	32.58	47.71
	20	68.94	8.56	6.54	15.96	32.67	43.83
	35	69.15	8.53	6.47	15.85	32.72	43.57
300	0	69.93	9.45	8.24	12.38	34.93	42.73
	10	70.67	9.38	7.82	12.13	35.12	54.64
	20	72.13	8.92	7.51	11.45	35.07	58.02
	35	72.96	8.85	6.53	11.67	35.21	59.38
330	0	69.98	8.47	8.07	13.47	33.35	30.79
	10	71.69	8.52	6.89	12.85	34.17	41.67
	20	72.17	8.61	6.69	12.53	34.46	51.45
	35	74.01	8.99	6.85	10.14	36.05	51.00

* Oxygen obtained by difference: 100% – C – H – N.

4. Conclusions

This study underscores the promising potential of hydrothermal liquefaction to obtain a valuable liquid biofuel precursor from digested secondary sludge. The resulting biocrude exhibits enhanced energetic density, with higher heating values ranging from 31 to 36 MJ kg⁻¹, increased carbon and hydrogen percentages, and a reduced oxygen percentage compared to the initial feedstock. The bioenergy recovery with the final product, reaching up to 59.38%, signifies the efficiency of the process. The investigation into the effects of various reaction temperatures and holding times on biocrude yield and quality revealed optimal conditions at 300 °C for holding times between 10 and 35 min, corresponding to biocrude yields of 20 – 21% with an energetic recovery surpassing 54%. However, the inherent variability in sludge origin and composition poses challenges in identifying universal reaction conditions for its conversion, crucial for the development of industrial-scale plants, that need to be robust and flexible. Despite these challenges, the hydrothermal liquefaction of waste biomass, such as sewage sludge, presents significant potential for enhancing waste valorization cycles, particularly when integrated with mature technologies like anaerobic digestion. Moreover, the obtained biocrude holds promise for integration into conventional processes for fuel upgrading, thereby partially meeting the demand for liquid fuels and contributing to a reduction in the carbon footprint of the sector. The potential of hydrothermal liquefaction in advancing sustainable development is substantial, contingent upon continued research and investment to overcome the current limitations of this technology.

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