**Energy valorisation of municipal sewage sludge for the production of renewable liquid fuels** **through the hydrothermal liquefaction process**

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**1. Introduction**

The growing energy demand, together with necessity to reduce greenhouse gases emissions related to the power sector, has led in recent years to an increasing interest in renewable energies sources, alternative to traditional fossil fuels. In this context, the municipal sewage sludge represents an interesting biomass to develop efficient waste-to-energy techniques to reduce the volumes and environmental impacts of wastes commonly disposed of in landfills. However, the solid content in the municipal sewage sludge (mainly constituted by proteins, carbohydrates and lipids) is typically in the range of 10–20%wt, and the energy content is low (higher heating value (HHV) of 10–25 MJ/kg on a dry basis). Thus, it is necessary to convert the organic matrix into high-energy-content fuels, in particular liquid ones required for many applications such as in the transport sector [1]. The production of bio-oil as liquid bio-fuel through the hydrothermal liquefaction (HTL) process is of particular interest, especially when applied to biomass with high moisture content, since the water in sub-critical state acts as solvent, catalyst, and reaction medium, and allows to convert the wet biomass into liquid fuels by processing it in a hot, pressurised water environment (250–350 °C and 15–220 bar). The HTL process enables the breaking down of the biopolymeric structure and the production of a liquid bio-oil as energy vector [2,3]. The target bio-oil is produced together with an aqueous phase, a bio-char and a gas phase [4]. In this study, HTL tests, carried out in batch autoclave reactors, were performed on a municipal sewage sludge to evaluate the yield of both the target bio-crude and other by-products at two different temperature levels.

**2. Methods**

The main properties of the municipal sludge used in this work are reported in a previous work [5]. Briefly, the sludge has a C, moisture and ash content of 34.6%, 12.1% and 21.2%, respectively, while its HHV is 13.5 MJ/kg. Prior to the HTL tests, the biomass was dried in an oven at 105 °C, until no change in weight was observed. HTL tests were carried out in a 500 mL Hastelloy C-276 batch reactor (Parr Instruments, series PA 4575A). The reactor was loaded with 30 g (dry basis) of a municipal sludge together with 270 mL of distilled water so to obtain a slurry with a 10%wt solid content, enabling to reproduce the typical sludge concentration value obtained downstream of wastewater treatment plants. Then, the reactor was purged four times with N2 at 5 bar to remove the O2 present in the vessel. The following stages are thereafter performed: i) first pressurisation stage with N2 fed; ii) second pressurisation stage at 200 bar by rapid heating of the system to the desired temperature; iii) running the HTL test at fixed temperature/time (300 °C and 350 °C – 20 min); iv) fast cooling of the reactor so to quench chemical reactions; v) depressurisation of the reactor. After the HTL test, the pressure difference measured between stages i) and iv) allowed to estimate the gas yield from van der Waals equation, considering that the produced gas is mainly composed by CO2 [2]. Then, the gas phase was vented to the atmosphere to restore ambient pressure and allow reactor discharge. The liquid and solid phases were recovered from the vessel with a spatula, and 30 g of dichloromethane (DCM) were added to maximise the products recovery. Subsequently, the slurry was filtered on a Büchner under vacuum. After filtration, the solid phase was subjected to a Soxhlet extraction with DCM to recover the bio-oil from the solid pores, while the liquid phase was separated into bio-oil and aqueous phase in a separating funnel. Finally, the bio-oil fraction obtained from the Soxhlet extraction and separating funnel underwent a distillation step with DCM (under vacuum at 30 ºC and 0.45 bar), and subsequently weighed to estimate its yield. The bio-oil, solid and gas yields *Y* were calculated according to, respectively:

$Y\_{bio-oil}= \frac{m\_{bio-oil}}{m\_{biomass, dafb}}∙100$ (1)

$Y\_{solid residue}= \frac{m\_{solid residue, db}}{m\_{biomass, db}}∙100$ (2)

$Y\_{gas}= \frac{m\_{gas}}{m\_{biomass, dafb}}∙100$ (3)

where *mbio-oil,* *msolid residue*, *mgas* and *mbiomass* represent the mass of bio-oil, solid residue, gas, and starting sludge, respectively. The subscripts *“db”* and *“dafb”* refers to dry basis and dry ash-free basis, respectively.

**3. Results and discussion**

Table 1 reports the effect of reaction temperature (300 and 350 °C) on the yields of bio-oil, solid residue and gas (taking into account that the gas produced by the HTL process is mainly composed by CO2) products at a fixed reaction time of 20 min. *Ybio-oil* and *Ygas* both increase by about 10% (in absolute terms) as the temperature rises from 300 ºC to 350 ºC. This result is likely linked to the favourable effect of the temperature increase in promoting the reactive pathways that determine the fragmentation of organic compounds to give the desired bio-oil and promote the production of gas via gasification reactions and secondary decompositions. Accordingly, the temperature increase determines a reduction of the solid residue yield from 33.6% to 25.9%. In this context, it should be emphasised that the solid fraction derives from multiple contributions: the inorganic fraction of the parent biomass (which could partially dissolve in the water medium as a function of the HTL conditions), an unreacted organic fraction of the starting matrix and the char fraction formed as a result of the HTL process through the recombination of free radicals.

**Table 1.** Yield of target bio-crude and other by-products at different temperature (runs perfomed in duplicate).

|  |  |  |  |
| --- | --- | --- | --- |
| HTL Temperature [°C] | Ybio-oil [%] | Ygas [%] | Ysolid residue [%] |
| 300  | 27.9 ± 1.4 | 5.6 ± 1.1 | 33.6 ± 0.9 |
| 350  | 38.3 ± 0.4 | 15.5 ± 1.1 | 25.9 ± 1.2 |

**4. Conclusions**

In this work, preliminary HTL tests were carried out on a municipal sludge to evaluate the yield of products at two different temperature levels. Best results were obtained in terms of bio-oil yield for the test conducted at 350 ºC where, on dry and ash-free basis, *Ybio-oil* is 38.3% with a relative increase of about 37% with respect to the test performed at 300 °C. On the other hand, higher temperatures also promote the formation of the gaseous phase, whose yield increase from 5.6% at 300 °C to 15.5% at 350 °C. Future studies will focus on a more detailed study of the effect of operating conditions on the bio-oil yield and quality.

**References**

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