

# Role of acid and basic pretreatment to prompt the real feasibility of hydrothermal liquefaction of a waste feedstock

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## Highlights

- The organic content of the pretreated SS is significantly affected by the pH of the pretreating solution.
- Biocrude yield increased from 19 up to 34 % wt at 350°C with HCOOH as pretreating agent.
- The H/C ratio of the biocrude goes from 1.67 to 1.85 is obtained with KOH pretreated SS.

## 1. Introduction

Hydrothermal liquefaction (HTL) could be a promising technology to produce biocrude from wet biomass. A conceptual analysis on the HTL of microalgae assisted by the use of solar heat demonstrated that even if microalgae are one of the most productive and investigated feedstock, their high cost hinders the economic sustainability of the process [1]. To overcome this issue zero-cost wet waste biomasses could be adopted with comparable efficiency. The variability of the matrix remains a significant challenge and opportunity for industrial HTL development. We studied the impact of pretreating real waste feedstocks to improve the quality of biocrude and enhance the plant's productivity, in terms of biocrude yield throughout the year due to the results of the conceptual analysis and the necessity to determine the economic sustainability of HTL.

## 2. Methods

SS provided by A.M.A.P. spa wastewater treatment plant of Palermo, Italy were used in HTL experiments as model waste feedstock. HCOOH and KOH were selected as pretreating agents. A slurry at 10%w/w of dry SS was used as feedstock. Batch runs were performed at 300, 350 °C for 30 min in an AISI 316 high-pressure reactor with an internal volume of 16 mL, processing 5 g of slurry in each experiment. The procedures adopted to separate the products downstream of HTL experiments were an optimization of those used in a previous work [2]. To study the effect of KOH and HCOOH, selected pretreatment trials were conducted using the same procedures adopted by Zimmermann et al. [3] in an AISI 316 batch vessel at 25 and 150 °C for 30 min. After the pretreatment the vessel was opened and all the content was poured in a flask and filtered on commercial filter paper to separate the solid residues from the eluted liquid phase. Ultrapure water (HPLC grade) was added to wash the residue from the additive till the pH of the filtrate was neutral. The filtrate liquid phase was analyzed by TOC. The solid residue was dried and a sample was calcined to estimate the organic content and a sample characterized by elemental analysis.

## 3. Results and discussion

The collected results revealed that the organic content of the pretreated SS is significantly affected by the pH of the pretreating solution. It ranges from 71 wt% (non-pretreated SS) to 55 %wt with KOH and to 82 wt% with HCOOH. In fact, as confirmed by some studies in the literature, the acid or basic solutions can interact with organic materials in the feedstock through several mechanisms [4-6]. HTL experimental runs of pretreated SS results in a higher biocrude yield, that increased from 19 up to 34 % wt at 350°C with HCOOH as pretreating agent. Moreover, it was found that the pretreatment step could affect also biocrude quality compared to non-pretreated SS across all temperatures tested. In fact a H/C ratio of the biocrude of 1.85 is obtained with KOH pretreated SS, that was significantly higher with respect the non-pretreated SS (1.67).

#### **4. Conclusions**

The results indicate that the efficiency of hydrothermal liquefaction of wet wastes could be enhanced through pretreating the feedstock. The pH of the pretreating solution impacts the organic content of the recovered particles, as shown by the varying HTL figures of merit based on the pretreatment agent utilized. Enhancing HTL productivity, specifically biocrude yield, is achievable by utilizing HCOOH for matrix pretreatment. Substituting HCOOH with KOH resulted in a greater H/C ratio of the biocrude.

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#### **Keywords**

Waste valorisation; sewage sludge; multiphase reaction; hydrothermal liquefaction.