

Hydrothermal liquefaction of waste: understanding of reaction pathways and implementation

Abstract

The production of advanced biofuels from waste biomass has gained much attention as a potential solution to the pressing issues of fossil fuel depletion and global warming. The hydrothermal liquefaction (HTL) reaction has exhibited intriguing capabilities in converting organic waste into oil under hydrothermal conditions (250-400 °C, 50-200 bar), with potential biofuel upgrading. Moreover, HTL has shown interesting preliminary results in the chemical and/or energy recycling of plastic waste. Although it has been observed that the nature of the feedstock significantly influences HTL performance, its impact on reaction mechanisms remains not fully understood. This thesis aims to enhance understanding of chemical reactions and interactions in HTL, enabling better tunability for diverse applications.

Initially, the study aimed to comprehend reaction mechanisms in the HTL of biomass by using monomers - glucose, glycine, and oleic acid – as representatives of the more complex bio-polymers - carbohydrates, proteins, and lipids, respectively. Experiments carried out in batch reactor showed a higher oil yield ('biocrude') using oleic acid, followed by glucose and glycine. However, the almost complete recovery of oleic acid in the oil-phase was explained by its inherently-like property. Unlike oleic acid, which showed very little reactivity in hydrothermal conditions, glucose and glycine underwent a plethora of reactions leading to the production of numerous chemical compounds, identified by HPLC, GC-MS, and μ -GC. Moreover, tests with binary and ternary mixture highlighted a strong interaction in the case of glucose-glycine, which leads to an increased oil production at higher temperatures, and higher solid and gas phase at lower temperatures. An experimental campaign based on consecutive reactions provided insight into the relationships present among the phases. Particularly, the interaction between glucose and glycine has been proven to be based on the formation of solid melanoidin-like compounds that degrade at high temperatures, forming nitrogen-containing aromatics that constitute the oil phase.

Subsequently, HTL of bio-polymers (cellulose, ovalbumin, and triolein) and real biomass was studied, focusing on the impact of the heating rate. Understanding the heating rate is crucial for real biomass and bio-polymers, as it can influence overall reaction selectivity through variations in the hydrolysis rate to monomers and the decomposition rate of these monomers and intermediates to the final products. Experiments showed that with long reaction times, the heating rate effect had limited effects, while significant changes were observed at shorter times. The variations in heating rate were explained by changes in the kinetic advancement of the reaction, with only minor differences being attributed to a direct influence of heating rate on reactive mechanisms.

Beyond biomass, synthetic polymers constitute a crucial waste category due to their global abundance, necessitating efforts to address their mismanagement. A possible valorization pathway is represented by chemical recycling, which is currently gaining momentum. In this context, HTL represents a promising technology. Despite very little being known about HTL of plastics, previous studies observed that heteroatom-containing plastic can be converted already in subcritical water into monomers and/or intermediates, while polyolefins require supercritical conditions. The different reactivity between these two classes of polymers could be exploited to efficiently valorize multilayer plastic films, a type of plastic waste whose recycling through current technologies is impossible. For this reason, their valorization by a double-

stage HTL process was studied in this work. Experiments conducted with a real PET-LDPE film at 325 °C allowed the isolation and recovery of 94% of terephthalic acid, one of the monomers of PET, leaving a solid residue constituted only by PE. This solid residue was then completely converted into gas-oily paraffinic hydrocarbons by reaction in supercritical conditions. The recovered terephthalic acid could be used for the production of virgin PET, while the paraffinic hydrocarbons can serve as feedstock for steam cracking to produce olefins for the petrochemical industry.

Another particularly important plastic polymer is PVC due to the challenges it poses, given the corrosivity and toxicity of the hydrochloric acid and dioxin it generates. This hampers the effective valorization of mixed post-consumer plastic waste, as PVC is frequently present. To address this issue, the feasibility of generating a chlorine-free solid for subsequent valorization in a hydrothermal environment was assessed, alongside a deeper understanding of the dechlorination mechanism. Almost complete dechlorination of PVC occurred at 300 °C in just 20 minutes, resulting in a solid residue with a 94% carbon yield, 86% energy recovery, and a predominant aromatic structure. Subsequent reactions under supercritical conditions produced hydrocarbons containing 30% of the initial PVC's carbon.

In the end, the industrial implementation of an HTL plant was assessed from both techno-economic (TEA) and life-cycle (LCA) perspectives. The study was focused on the coupling between an HTL plant and an aqueous phase reforming (APR) section, as possible way to valorize the residual aqueous phase. APR allows the catalytic conversion of the residual oxygenated compounds present in the aqueous phase into hydrogen that can be used for the in-situ upgrading of the biocrude into drop-in biofuel. Two case studies were evaluated, based on two different lignocellulosic feedstocks, i.e., corn stover (CS) and lignin-rich stream (LRS). The resulting minimum selling price for the biofuel was within 1.23-1.27 €/kg, while the global warming potentials (GWP) was within 41-47 g CO₂ eq/MJ biofuel, consisting in a substantial reduction with respect to fossil diesel. Interestingly, the implementation of APR was particularly profitable with CS, as it produced 107% of the hydrogen required for biocrude upgrading, while it was limited to 19% for the LRS case. This indicates that the HTL-APR coupling can be a useful process for producing greener hydrogen to be used in situ, but its effectiveness is strongly dependent on the feedstock's performance during HTL.