Hydrothermal Liquefaction of oleaginous yeast targeting intermediate biofuels production

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Oleaginous feedstocks (microalgae and yeasts) are able to accumulate significant quantities of lipids in a low period of time. The lipid content can reach up to 70%wt of the cell's mass, which includes mainly fatty acids. So, this type of biomass has the potential to replace animal fats, as well as vegetable oils, as raw materials for the production of renewable fuels. Also, these types of feedstock belong to wet biomass category as they are grown in water medium, so they can be thermochemically converted via Hydrothermal Liquefaction (HTL) without needing to extract the lipids or dry the materials. By doing this, the cost of the conversion process is limited and the process is eco-friendlier. Thus, in the present study, two different strains of high-lipid oleaginous yeasts (Cryptococcus Curvatus and Lipomyces Starkeyi) are tested as HTL raw material for the production of bio-crude oil, a biofuel intermediate product.

The study examines comparatively the HTL process on the two oleaginous yeasts both in terms of bio-crude oil yield and properties. It is worth mentioning that both feedstocks are consisted of high lipid content (>50wt%) and very low ash content. In the first step, the process is optimized for every biomass type to achieve maximum oil production by evaluating the three main parameters which are temperature, residence time and feed-to-solvent ratio. The temperatures examined are in the range of 280° - 350°C, residence time between 5 and 60 min and the ratio of biomass/solvent in the range of 1/5 up to 1/20. The experimental study is conducted at the Centre for Research & Technology Hellas (CERTH) in a bench top, batch, high-pressure stirred reactor with an internal vessel volume of 250 mL (Parr 4576A). The plant is equipped with a J type thermowell for heating the reactor and a U type cooling coil for temperature control and rapid dropping after the end of the process. During a single run, the reactor is loaded with 10g of feedstock (in 1/10 biomass/solvent ratio) and 100 mL of deionized water. Then, the reactor is sealed and purged 3-4 times with compressed nitrogen to remove inert air. Finally, the reactor inlets are compressed to 30bar with nitrogen (to achieve inert atmosphere and preserve liquid state during heat-up), then heated and kept to the corresponding temperature according to the applied set of conditions for a specific amount of time prior to its cooldown to ambient temperature.

Hydrothermal liquefaction of biomass leads to the production of solid, liquid and gas products due to the biomass decomposition. During the decompression of the reactor a gas sample is collected in a tedlar bag in order to be analyzed via GC-FID. The collection of the solid and liquid products initiates with the vacuum filtration of the mix in a Buchner funnel equipped with a filter paper. The collected liquid stream is the aqueous phase product, as it contains the applied solvent along with a part of liquified water-soluble organic molecules. Then, the remaining viscous mix in the filter paper is rinsed with 300 - 500 mL of acetone to separate the bio-crude oil from solids (solid residue) and collect it in the Buchner flask. The remaining solids are dried overnight in an oven and weighted, while the organic mix with acetone is subjected to rotary evaporation at 40°C under reduced pressure to collect the final bio-crude oil product and extract the used acetone. The process is depicted on the following figure.

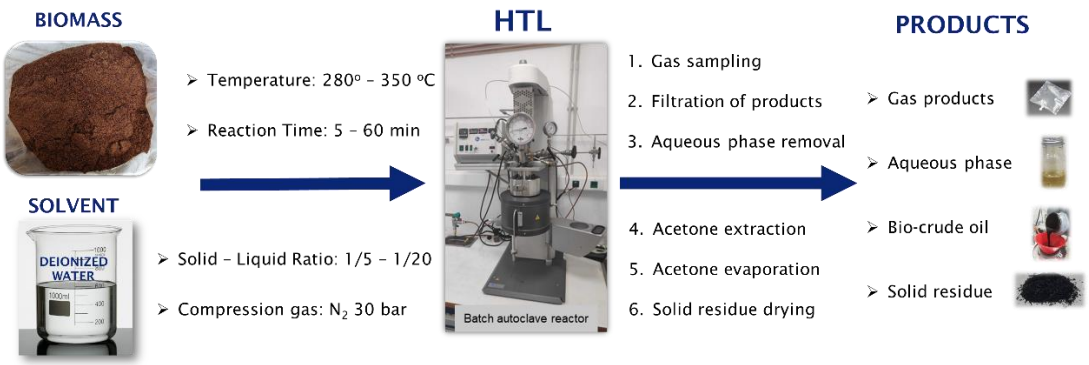

Figure 1. Hydrothermal liquefaction process methodology

The study, which is still in progress, has some initial conclusions been drawn. HTL of Lipomyces Starkeyi leads to a high production of bio-crude oil (>60wt%) while the solid residue yield is very low (<5 wt%). Residence time, as well as temperature, affect the oil yield synergistically. The evaluation of the HTL process is currently limited to Lipomyces Starkeyi yield results and some preliminary quality tests conducted on the bio-crude oil. Regarding the HTL of Lipomyces Starkeyi, in Figure 2 the impact of the applied temperature and residence time on the bio-crude oil yield is depicted. The main conclusion extracted from the results is that temperature and residence time apply synergistically on the bio-crude oil yield. At 280°C, 300°C and 320°C the yield is increased from 15 to 30min and is decreased at 60min. However, at 350°C the ideal residence time is at 15min because of the severity of the applied temperature. At 15min residence time, the optimum bio-crude oil yield is obtained at 350°C while at 30 and 60min it is achieved at 300°C and appears to decrease above this point. So, both parameters affect equally and in cooperation the conversion of the yeast cells into liquid organic molecules. Moreover, the bio-crude oil yield is generally high in all sets of parameters (60 – 67wt%) which can be attributed to the high lipid content of the cells. The oil yield compared to other lignocellulosic materials HTL (30 – 40wt%) is significantly higher meaning that oleaginous cells appear as suitable feedstock to produce biofuel intermediate high value products. As lipids are mainly comprised of fatty acids, they can get effectively decomposed into their units at high rates which are also water in-soluble molecules and are mitigated to bio-crude oil product. Therefore, this is the main reason that the yield is so high as almost all lipids are liquified along with a small proportion of nitrogenous compounds derived from proteins and some degraded carbohydrates.

The optimal set of conditions was found to be 300°C and 30min residence time with yield of 67wt%. In the optimal condition the elemental content analysis showed high proportion of Carbon (~70wt%) and Hydrogen (~11wt%) and very low Nitrogen (~0.2wt%). So, the produced bio-crude oil has enhanced elemental content and high heating value (~36MJ/kg) that renders it suitable for the production of biofuels. The study is also expected to comparatively study the effect of parameters in the two types of yeasts and also to determine the impact on the products quality. The gas product is studied via GC-FID and the aqueous phase is examined for its carbon (via elemental analysis) and sugars content (via HPLC). The bio-crude oil which is the main product is subjected to elemental analysis (C, H, N, O, S), calculation of Higher Heating Value (HHV) and energy recovery, gas chromatography to determine the structure of the liquefied molecules and thermogravimetric analysis for comparison to conventional fuels boiling point range. So, by the end of the study it is expected to be able to optimize the process for each type of oleaginous yeast, determine the yield of the products and understand the network of reactions that occur during the process.

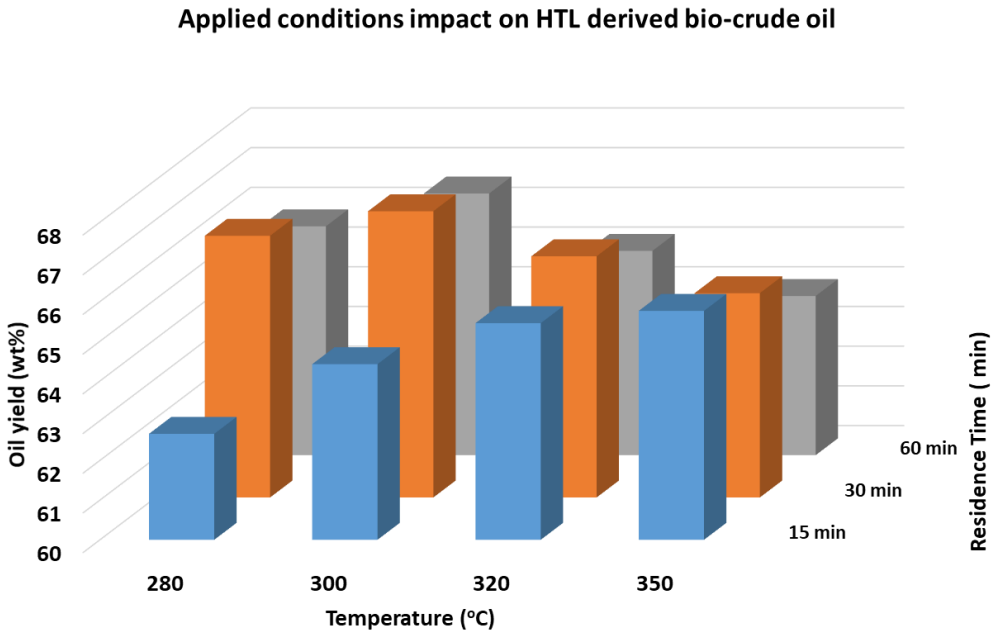

Figure 2. Effect of temperature and residence on bio-crude oil yield