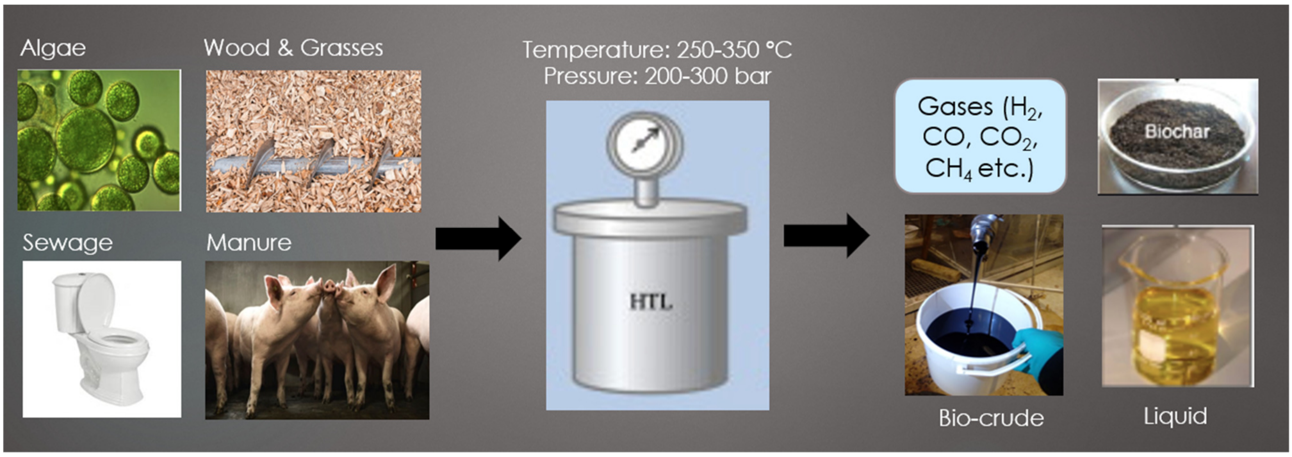
Hydrothermal liquefaction of biomasses - quantitative analysis of bio-crude

Hydrothermal liquefaction (HTL) is a promising process for converting biological materials (such as microalgae, grass and waste) into biofuels and value-added chemicals.

HTL exploits the unique properties of hot compressed water by employing conditions of 250-350 °C and 200-300 bar pressure. The use of water as a reaction media makes HTL highly flexible to diverse feedstocks with the only requirement that it can be suspended in water for effective pumping at high pressure. The feedstock flexibility has been demonstrated in batch experiments where numerous biomasses have been explored, including lignocellulosics (e.g., Miscanthus, pine, willow, aspen, bagasse, spent coffee ground), microalgae (e.g., Spirulina, Chlorella pyridenosa), macroalgae (e.g., Laminaria hyperborean), and residues (e.g., manure, sludge, digestate, pomace, dairy effluent).



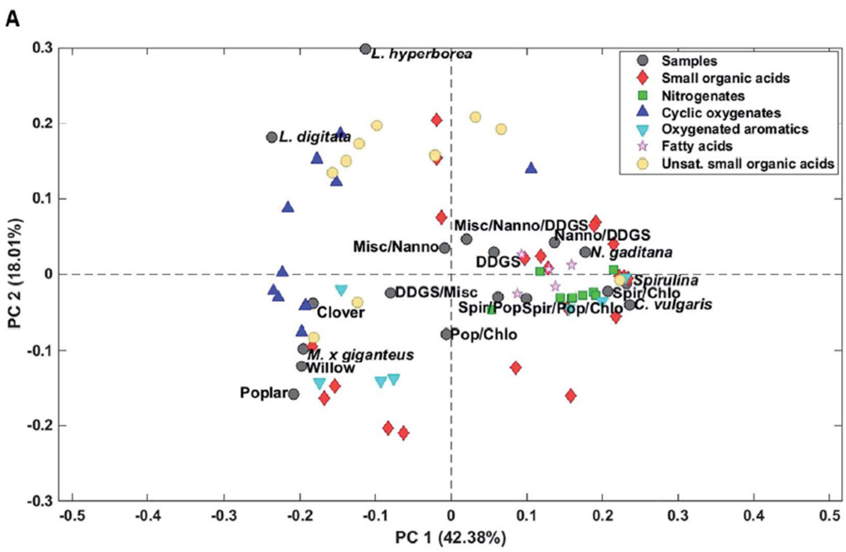
HTL experiments can be conducted in small 20 mL batch reactors. Reactors are loaded with biomass, filled with demineralized water and mixed in the reactors. The reactors are sealed and lowered into a fluidized sand bath preheated to the designated temperature. The reactor is then cooled and the products are separated. The process results in four phases: a bio-crude phase, water phase, gas phase and solid residue. The bio-crude phase is of particular interest, since it can be upgraded to advanced fuel-oil. The liquid phase contains value added chemicals that can be used in industrial application. The gas phase contains mostly H_2, CO, CO_2 and CH_4 and finally the solid residue also called biochar, can be used as fertilizer.

The biochemical composition of the feedstock is one of the most important contributing factors of bio-crude yields and composition, while temperature, reaction time and solid loading have lesser but still significant effects. Design of Experiments (DoE) can be used to explore the most important variables in HTL. In DoE we deliberately change one or more variables in order to observe the effect the changes have on the response. Well chosen experimental designs maximize the amount of 'information' that can be obtained from a minimum amount of experiments. To explore the effect of temperature, reaction time and solid loading a circumscribed central composite design (CCD) can be employed instead of using the one-at-a-time approach, where you only vary one variable at a time.

Characterization of the aqueous phase and bio-crude are of interest. Extensive quantitative analysis is important for understanding potential effects and possibilities for use of the two phases. Predictive models for the composition and properties would thus be of substantial benefit and provide means for adjusting the phases for optimal use. The vast majority of compounds reported for bio-crude from HTL studies contain one or more heteroatoms. Especially the presence of nitrogen is problematic due to the formation of NOx gases upon combustion and difficulties with hydro-denitrogenation during upgrading. A variety of advanced analytical techniques has been applied to investigate the composition of the biocrude, including FTICR-MS, NMR, SEC, GC-MS and pyrolysis-GC-MS.

The volatile and semi-volatile components of the bio-crudes and standard solutions have been analyzed with GC-MS (gas chromatography-mass spectrometry) with prior derivatization. Bio-crude is dissolved in dichloromethane and MSTFA along with an internal standard. Analysis is then performed using an Agilent 7890B GC coupled to a quadrupole mass filter MS (Agilent 5977A).

After GC-MS analysis analytes in the bio-crude samples using different programs, e.g. MassHunter. Principal Component Analysis (PCA) is often used as an exploratory method to gain an overview of multivariable data in the form of groupings, correlations, or outliers. Hence, similarity or dissimilarity of samples can be evaluated. PCA makes data easy to explore and visualize



Madsen et al. "Hydrothermal co-liquefaction of biomasses - quantitative analysis of bio-crude and aqueous phase composition." Sustainable Energy and Fuels, 2017, 1, 789.