



Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition



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HIGHLIGHTS

- Hydrothermal liquefaction water recycle increases bio-crude yields significantly.
- Biomass to bio-crude energy recovery reaches 95%.
- Non-catalytic HTL reduces bio-crude oxygen content.
- Bio-crude water content increases with use of K_2CO_3 .
- Recycling results in concentration of organics in water.

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ABSTRACT

Hydrothermal liquefaction (HTL) is a promising thermo-chemical processing technology for the production of biofuels but produces large amounts of process water. Therefore recirculation of process water from HTL of dried distillers grains with solubles (DDGS) is investigated. Two sets of recirculation on a continuous reactor system using K_2CO_3 as catalyst were carried out. Following this, the process water was recirculated in batch experiments for a total of 10 rounds. To assess the effect of alkali catalyst, non-catalytic HTL process water recycling was performed with 9 recycle rounds. Both sets of experiments showed a large increase in bio-crude yields from approximately 35 to 55 wt%. The water phase and bio-crude samples from all experiments were analysed via quantitative gas chromatography–mass spectrometry (GC–MS) to investigate their composition and build-up of organic compounds. Overall the results show an increase in HTL conversion efficiency and a lower volume, more concentrated aqueous by-product following recycling.

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1. Introduction

Hydrothermal liquefaction (HTL) is emerging as an innovative technique for production of liquid transportation fuels. In HTL, high temperature and pressure is applied to biomass feedstocks in aqueous slurries, resulting in a liquid raw product similar to petroleum crude, for this reason termed bio-crude. This bio-crude can be further upgraded and used as co-feed for conventional refinery processes or directly refined into drop-in fuels. HTL has the advantage of being a wet processing technique, meaning feedstocks do not have to be dried, making it particularly attractive for wet feedstocks. Therefore research into HTL has often focussed on the production of bio-crude from the third generation bioenergy feedstock microalgae (Elliott, 2016). Microalgae have a potentially high area

specific growth yield and can exhibit high lipid contents which make them attractive as a feedstock. However, the scalability of microalgae cultivation is still in its infancy and developments are not progressing as fast as the HTL technology itself. Therefore focus is shifting to biomass and waste feedstocks with high availability such as lignocellulosics, agricultural wastes, macroalgae, DDGS and bio-solids. Most feedstocks are naturally wet upon harvesting or procurement; for example lignocellulosics have a moisture content of around 50% upon harvesting. Grasses generally have a moisture content of 60–85%, macroalgae around 70–90% and wastes such as sewage sludge, manures and digestate of around 90% (Wachendorf et al., 2009; Wang et al., 2011). Some of these feedstocks are procured at solids loadings directly suitable for HTL (~20 wt%), however particularly lignocellulosics are likely to require addition of water to obtain a pumpable slurry. This is particularly true if a pre-treatment and size reduction technique is employed which requires relatively dry biomass. To produce a

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pumpable slurry for HTL, addition of water would be required which is undesirable due to cost and environmental footprint. Therefore re-use of the aqueous by-product from HTL has been suggested to provide the aqueous media for subsequent HTL runs. Since all HTL feedstocks contain at least some moisture and usually at least 50%, production of a waste water stream is inevitable. Not all water can be recycled as the solids concentrations would drop due to dilution with the biomass moisture content. Nevertheless, recycling leads to a reduction of volume of waste water. This is expected to have both an environmental and economic advantage. It also has the advantage of concentrating organics in the water phase, this consequentially increases the viability of energy production from the water by-product. Hydrothermal gasification of the aqueous phase has been suggested as a means to recover energy in the form of methane for process integration (Elliott et al., 2015, 2013). High temperature hydrothermal gasification has also been suggested for the production of hydrogen to fulfil demand required for hydrogenation of the bio-crude (Cherad et al., 2016). Both these routes will greatly benefit from higher organics loading in the water due to increased thermal efficiency as more energy can be produced per volume of water due to the increased concentration. Similarly, anaerobic digestion (AD) could benefit in the same way although this is a less researched route for HTL process water. To our knowledge, only one study to date has assessed the use of HTL process water for methane production via AD, and showed it was possible but remove up to 61% COD with an anaerobic biodegradability of up to 84%, however it was pointed out that phenolics and cyclic hydrocarbons led to a lag phase and a reduced production rate (Tommaso et al., 2015). Therefore the accumulation of such inhibitory compounds should be monitored closely upon water phase recycling.

Water phase recycling has been mentioned in various publications to be a necessity for large scale industrial HTL applications but has only been investigated to a very limited extent in the literature. Three studies investigated water phase recycling in batch reactors for desert shrub, microalgae and barley straw, one study employed continuous HTL with water phase recycling using aspen wood (Li et al., 2013; Pedersen et al., 2016; Ramos-Tercero et al., 2015; Zhu et al., 2015). Further studies by the Pacific Northwest National Laboratory (USA) have also reportedly employed water phase recycling but no mention or analysis of its effect is presented (Zhu et al., 2014). Generally all studies observed an increase in bio-crude yield and organic carbon loading in the water phase. Li et al. (2013) for example found that the heavy oil yield from *Salix psammophila* (desert shrub) increased from 30 to 47% after three rounds of process water recycle (Li et al., 2013). In a similar study using three rounds of recycle Zhu et al. (2015) observed a minor increase in bio-crude yield from 35 to 38% (Zhu et al., 2015). The work by Ramos-Tercero et al. (2015) extends the number of recycle experiments to a total of 7 and also investigated three different temperatures. At each temperature (220, 240 and 265 °C) recycling led to significant bio-crude yield increases. The extended recycling trial to seven rounds showed a steady increase up to 42% from the original 15% (Ramos-Tercero et al., 2015).

Pedersen et al. (2016) co-liquefied aspen wood with glycerol and performed three consecutive recycling stages of the water phase on a continuous bench scale HTL unit (Pedersen et al., 2016). The results showed a large increase in total organic carbon from 54 to 136 g/L and an increase in ash content in the water. The effect on bio-crude yields is less apparent in this study due to high experimental variability, probably caused by the much larger continuous system compared to the previously mentioned small batch studies. The Pedersen et al. (2016) study used K₂CO₃ homogeneous catalysts at 4.2 wt% of slurry and additional catalyst was added to each recycling stage. It was shown that this led to an increase in ash content of the water phase. It is generally accepted that HTL

requires alkaline conditions if the amount of solid residue is to remain small since alkali catalysts reduce char formation, particularly from carbohydrates (Biller and Ross, 2011; Zhu et al., 2014). It is apparent that adding additional catalyst in each HTL cycle will lead to an increase in inorganics in the systems and potentially an increase in solid residue and ash formation. Therefore one of the focuses in the current study was to assess the effect of K₂CO₃ homogeneous catalyst on the recirculation of HTL waters. This is the first time such a comparative study has been performed and additionally the recirculation to a total of ten subsequent cycles is evaluated, further than any previous studies. The present work extends the current literature and knowledge in the field by comparing catalytic and non-catalytic process water recycling with up to 10 rounds and quantitative analysis of the bio-crudes and water phase.

2. Materials and methods

2.1. Hydrothermal liquefaction and sample work up

The HTL feedstock, dried distillers grains with solubles (DDGS) is a by-product from ethanol production and was obtained from Agroethanol, Närke, Sweden. Feedstock analysis revealed a biochemical composition on a dry and ash free basis of: 35.0 ± 1.3 wt% carbohydrate, 42.2 ± 2.2 wt% protein, 22.4 ± 0.3 wt% lipid and 2.8 ± 0.1% lignin. The analytical methodologies for protein, carbohydrate and lipid analysis are described elsewhere (Biller and Ross, 2011). Lignin content was measured using the acetyl bromide method upon extensive washing to remove proteins (Moreira-Vilar et al., 2014). K₂CO₃ the homogeneous catalyst for HTL was obtained from Sigma Aldrich.

For each HTL experiment DDGS was mixed with or without K₂CO₃ and water (or recycled water) on a mass basis of 78% DDGS, 2% K₂CO₃ and 20% water/recycled water. For the non-catalytic experiments the amount of DDGS was adjusted to 80% with 20% water. Continuous HTL experiments were carried out using the reactor described in detail previously, for a full description of and a schematic of the reactor we refer to the previous publication (Mørup et al., 2015). Continuous HTL was performed for a catalytic baseline experiment and two sets of recycle, from here on in described as direct catalytic continuous (DC1 cont), recycle catalytic continuous 1 and 2 (RC1 cont, RC2 cont). The focus of the current work was to perform additional recycle experiments and compare to the non-catalytic recycling. For this purpose batch reactors were employed, because the continuous reactor requires large amounts of water to reach steady state, resulting in less and less water phase being available for the next recycle experiment. This is why only 2 recycles could be employed on the continuous system.

HTL batch reactions were carried out in custom build Swagelok bomb type reactors. The reactors were constructed from 316 stainless steel 3/4 inch Swagelok pipes. One side of the reactor was capped and the other side connected to a 3/4 – 1/4 inch reducer. A 3 cm, 1/4 inch pipe was connected to the reducer and capped at the other end. This 1/4 inch cap was used to vent the reactors rather than a 3/4 inch fitting. The 3/4 inch pipe had a length of 10 cm, resulting in a total reactor volume of 20 mL.

The reactors were submerged completely into an OMEGA FSB-3 fluidised sand bath via a steel chain linked to the reactor with a carabiner. The fluidised sand bath temperature was set to 350 °C. An internal thermocouple inside the reactors showed that the temperature inside the reactor reached a maximum of 340 °C, this final temperature was reached within 4 min. Once the desired residence time of 20 min (including heat up time) was reached, the reactor was quenched in a cold water bath. Once cold, the reactors were

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