

Hydrothermal Carbonisation of Spent Coffee Grounds and Subsequent Anaerobic Digestion of Process Water

B.S.Campbell¹, R.B.Thorpe¹, D.Peus², J. Lee¹

¹Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2 7NU, UK

²Antaco UK, Lantern House, Walnut Tree Close, Guildford, GU1 4SW, UK

Keywords: Spent Coffee Grounds, Hydrochar, Biogas, Valorisation.

Presenting author email: bethany.campbell@surrey.ac.uk

Spent coffee grounds (SCG) are a major waste stream globally, with approximately 6 million tonnes of them produced each year (Tokimoto *et al.*, 2005). Their high organic content means they produce high amounts of CO₂ and CH₄ when allowed to degrade in landfill, and this organic content can be recovered as renewable energy. An option for this recovery is hydrothermal carbonisation (HTC) - a hydrothermal conversion technique that can produce useful carbonaceous products from wet biomass. The main benefits embodied by this hydrothermal technique are improved dewaterability and energy densification (Zhao *et al.*, 2014), producing a solid fuel that can replace coal in power stations, and efficient phosphorus recovery (Crossley *et al.*, 2020). However, the production of large volumes of contaminated process water represents a challenge when looking to utilise HTC on an industrial scale. With 15-20 % of the input carbon dissolved in the liquid phase, the resulting process water has high chemical oxygen demand (COD) – upwards of 17,530 mgO₂/L (Ramke *et al.*, 2009; Danso-Boateng *et al.*, 2015), so for good overall energy recovery, this needs to be captured. HTC has been used for the treatment of SCG to produce hydrochar as an improved fuel (Kim *et al.*, 2017), as specialised activated carbons (Khataee *et al.*, 2017; Querejeta *et al.*, 2018), and the solid used to improve anaerobic digestion (Codignole Luz *et al.*, 2018). In the study of SCG-based hydrochar, the process water has not been considered but constitutes a substantial product from HTC with high carbon loading which needs to be investigated. This paper looks at both the HTC of SCG, as well as the utilisation of anaerobic digestion of untreated process water to reduce the COD of the process water and, at the same time, to recover the carbon as biogas, which can be used to help power the system.

In this work, 60 g of dried SCG were mixed with 540 ml DI water to produce a 10 wt% DS mixture. This mixture was heated in a sealed 1000 ml autoclave for 5 hours under typical HTC conditions of 200°C under autogenic pressure. The mixture was allowed to cool overnight, the residual head pressure noted, and resulting slurry was discharged and separated by vacuum filtration. The process water was collected and stored in the fridge, and the char washed with 1L DI water before drying at 90 °C. The char and process water carbon contents were measured, and the process water was analysed for COD content. Anaerobic Digestion was undertaken in an Electrolab BIOTECH 5L Fermenter Reactor using 1.5 L inoculum. 3.5 L of DI water were added, resulting in a mixture with a Total Solids (TS) content of 1.22 wt%, with a volatile solids (VS) content of 59.3 % (0.72 wt%). For start-up, the digester was fed with 1 g/L glucose once a week for two weeks, before daily feeding of fresh (< 5 days old) HTC process water was initiated at an average organic loading rate (OLR) of 0.4 gCOD/L/day, giving a hydraulic retention time (HRT) of 75 days. Effluent was removed daily from the centre of the stirred reaction vessel, and influent added subsequently to the bottom of the vessel to retain a constant reaction volume. Biogas was collected and measured in a measuring cylinder using water displacement, and then transferred to a gas bag for weekly analysis. Process water influent COD and pH were monitored, and digester effluent was filtered through a 0.22 µm filter before pH, COD and TOC analysis. Process stability was monitored using the volatile fatty acid – total alkalinity ratio (VFA/TA - Ripley ratio) through titration of 200 ml of 10x diluted effluent with 0.05 M H₂SO₄ to a pH of 5, then further to a pH of 4. After 90 days of feeding, the OLR was doubled, reducing the HRT to 37 days, and the OLR was subsequently reduced again after a further 35 days. When pH was determined to be too low, Na₂CO₃ and NaHCO₃ were added in distilled water, after removal of the equivalent volume of effluent.

The hydrothermal carbonisation of spent coffee grounds gave a 56 ± 3 % solid yield, with a carbon yield into the hydrochar of 81 ± 8 %, and carbon dissolution into the process water of 16 ± 7 %, in line with carbon yields in the literature (Berge *et al.*, 2011; Afolabi, Sohail and Cheng, 2020). A small amount of gas is also produced during the hydrothermal carbonisation, resulting in a residual head pressure of 2.8 ± 0.6 bar in the reaction vessel after cooling; this is assumed to be all CO₂, from the decarboxylation in HTC. The COD of the process water was 33,700 ± 2,668 mgO₂/L and the pH was 3.92 ± 0.07; an acidic pH is expected due to the known breakdown of carbohydrates in the HTC reaction, resulting in the production of organic acids (Wang *et al.*, 2018).

After just three days of feeding HTC process water, the absolute COD in the digester deviated below the theoretical COD (as predicted by the influent concentration, given no COD degradation), and methane was being produced (Figure 1), signalling the degradation of COD into methane, and likely the growth of biomass. However, the mono-digestion of the process water took about 43 days to reach a steady-state with an average methane production of 0.17 L/gCOD fed, a similar level to that seen in the mono-digestion of process liquor from HTC of sewage sludge (Wirth, Reza and Mumme, 2015). Before this, there were issues with falling pH, reaching 5.83 on day 10, and an increasing VFA/TA ratio reaching 2.84, signalling the increase of acidity in the digester and severe

digester instability. Stable digester pH should remain between 7.0 and 8.5, and VFA/TA between 0.10 and 0.35 (Lafratta *et al.*, 2020), as low pH and high organic acid content can inhibit methanogenic bacteria. However, the addition of alkalinity successfully increased the pH and reduced the VFA/TA ratio to stable values of > 6.48 and < 1.12 , respectively, over the steady state period. These values would normally still indicate too high VFA content, but the good methane production indicated relative process stability. It was hypothesised that the complex nature of the process water fed, and possible other buffering systems than the carbonate measured in the Ripley Ratio, such as phosphate buffering, maintained stability. However, following increase of the organic loading rate at day 90, the methane yield dropped significantly, along with the pH, and further addition of alkalinity was not able to return the prior methane production. This was attributed to the sheer loading of organic acids in the process water, which could not be overcome by the buffering capability of the system and additional carbonate. The organic loading rate was again reduced, in order to try and restore the previous steady state and methane production, but the methane yield remained at 0.01 L/gCOD.

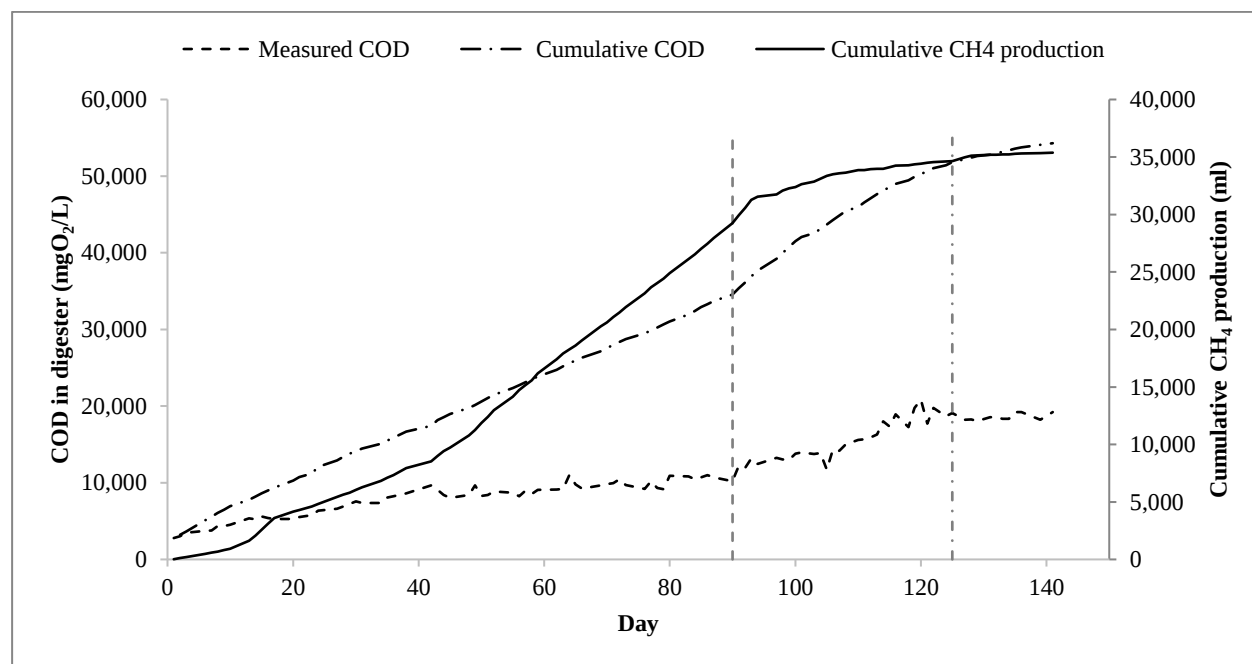


Figure 1: Chemical oxygen demand (COD) content in the anaerobic digester based on effluent concentration, theoretical COD content based on influent concentration given no COD degradation, and cumulative methane production. The dashed vertical line indicates the increase of organic loading rate, and the dashed and dotted vertical line indicates the reduction of organic loading rate.

The combination of hydrothermal carbonisation and subsequent anaerobic digestion is a good option for the recovery of carbon from spent coffee grounds with 81 % of the carbon captured in the hydrochar, and a large proportion of the carbon solubilised into the aqueous phase valorised as high-quality biogas. Process stability of anaerobic mono-digestion of process water was good at low organic loading rate, but the high levels of organic acids in the water caused issues with process stability at an increased organic loading rate, resulting in reduction in methane production. Work to reduce the remaining organic content to a level suitable to discharge will continue to be investigated.

- Afolabi, O. O. D., Sohail, M. and Cheng, Y.-L. (2020), *Renewable Energy*. 147, pp. 1380
- Berge, N. D. *et al.* (2011), *Environmental Science and Technology*. 45(13), pp. 5696
- Crossley, O. P. *et al.* (2020), *Bioresource Technology*. 301, 122664.
- Danso-Boateng, E. *et al.* (2015), *Bioresource Technology*. 177, pp. 318
- Lafratta, M. *et al.* (2020), *Bioresource Technology*. 310, 123415.
- Ramke, H.-G. *et al.* (2009) *Hydrothermal Carbonization of Organic Waste*. Available at: http://wwwwdev.hs-owl.de/fb8/fachgebiete/abfallwirtschaft/pdf/Sardinia_2009_HTC_Internet.pdf
- Wang, T. *et al.* (2018), *Renewable and Sustainable Energy Reviews*. 90, pp. 223
- Wirth, B., Reza, T. and Mumme, J. (2015), *Bioresource Technology*. 198, pp. 215
- Zhao, P. *et al.* (2014), *Energy Conversion and Management*. Pergamon, 78, pp. 815