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White paper: PFAS elimination by Pyrolysis

Background

Per- and poly flourinated substances (PFAS) are known as forever chemicals as they are very difficult to break down in nature. They are of high concern, with some being carcinogenic, hormone disruptive, and with negative reproductive and developmental effects. There are more than 8000 PFAS compounds and only a few of the oldest and most common (perflouro octane sulfonic acid (PFOS), perflourooctanoic (PFOA)) are now prohibited to produce and use.

This paper is showing how pyrolysis can eliminate the PFAS content in the biochar and flue gas produced from sewage sludge including listing evidence of PFAS degradation at conditions present under AquaGreen's process conditions with pyrolysis at 650 °C for 20 min and subsequent thermal oxidation at 900-1000 °C.

Literature review and resulting hypothesis

A 2021 state of science review article reports *"**The basic pathway for thermal PFAS destruction in a reductive environment is hydrodefluorination** (HDF)..HDF is the conversion of a carbon-fluorine (C–F) bond into a carbon-hydrogen (C–H) bond"*[1]*.* This is the case for AquaGreen's biosolids pyrolysis, where hydrogen is present in the pyrolysis gas. This may be a key reason for PFAS degradation occurring at lower temperatures during pyrolysis compared with combustion as the degradation pathway is different.

A study has shown that 99.6 % of PFOS is degraded at 600 °C and 99.95 % at 900 °C in lab trials [2]. Hence while it is often reported that temperatures above 1200 °C is required for PFAS degradation this is not the case for PFOS, which is the main PFAS contaminant in Danish sewage sludge samples[3].

AquaGreens plant has a thermal oxidizer burning all the pyrolysis gases at 900-1000 °C. The state of art review by Winchell et. al. also underlines its role in the PFAS degradation. *Thermal oxidizers are often permitted for 99.99% emission reduction, and a recent test report of a thermal oxidizer used to control PFAS process stream emissions from an industrial facility demonstrated compliance with this requirement (Focus Environmental Inc., 2020). **Consequently, the critical step for achieving PFAS control in pyrolysis and gasification systems may be the operation of the downstream thermal oxidizer**[1].*

This hypothesis is further supported by the results of Bioforcetech and the Environmental Protection Agency in USA. They have shown **PFAS degradation** to **non-detectable level in both biochar**[4,5] **and flue gas and scrubber water emissions**[6,7] with **pyrolysis at 600 °C for 20 minutes**

and subsequent thermal oxidation at 850 °C at a full-scale pyrolysis plant in California, USA. For the Flue gas FTIR analysis was performed to detect 18 C1-C8 PFAS components. They were all below detection limit.

The thermal process of AquaGreen is similar to Bioforcetech's, with the notable difference that AquaGreen pyrolyse at 50 °C higher temperature, and control the thermal oxidation at 900-1000 °C.

Sandblom (2014) hypothesized that any PFAS compound escaping the furnace (of a Sewage sludge incinerator) *would be captured in the wet scrubber due to their low pKa values*[1]. Based on this - if we do not recover any PFAS in the scrubber water in the AquaGreen plant at Fårevejle, this will also indirectly point to PFAS destruction in the pyrolysis and thermal oxidation in the burner.

PFAS removal by pyrolysis - trials at Fårevejle wastewater treatment plant in Denmark

Based on the above AquaGreen, Odsherred Utility Company and Envafors Utility company conducted PFAS measurements on the drying and pyrolysis of sludge from the 2 utility companies. In two trials in April-May 2022 Eurofins analyzed the biochar and the water streams for the 22 PFAS compounds listed by the Danish EPA. PFAS analysis of flue gas was not available in Denmark at the time of the trials (April-May 2022). A third trial drying and pyrolysing sludge from Odsherred Utility Company, with PFAS measurements also on the flue gas, was carried out October 2022.

Results drying and pyrolysing sewage sludge from Odsherred Utility Company, Denmark

The sludge from Odsherred Utility company had a PFAS level below the guiding limits of the Danish EPA of 10 µg/kg dry matter. It contained 3,9 µg/kg dry matter PFOS, 4,3 µg/kg dry matter PFAS4 and 6,8 µg/kg dry matter PFAS22, and in total 6 of 22 of the PFAS compounds listed by the Danish EPA were detected[8].

In the October 2022 trials biochar and flue gas was analysed by Eurofins both before and after the scrubber. 32 PFAS compounds were included in the flue gas analysis with individual detection limits from 0,003 – 0,005 µg/Nm^3.

The biochar produced from the biosolids is PFAS free[9]. The flue gas is PFAS free both before[10] and after[11] the scrubber.

Results drying and pyrolysing sewage sludge from Envafors Utility Company, Denmark

The sludge from Envafors Utility company is considered contaminated in Denmark containing 49 µg/kg dry matter PFOS, 52 µg/kg dry matter "PFAS4" and 57 µg/kg dry matter "PFAS22", and in total 8 of 22 of the PFAS compounds listed by the Danish EPA are detected[12].

The biochar produced from the biosolids is PFAS free[13].

The scrubber water and condensate were found to have the same level of PFAS22 as the technical water used in the process, with a concentration of approximately 30 ng/l[14].

There was no additional PFAS from the biosolids in the scrubber water pointing to complete destruction of any remaining PFAS22 compounds in the thermal oxidation in the AquaGreen burner.

This matches the hypothesis listed in the literature mentioned above. The results of October 2022, where no PFAS is detected in the flue gas before the scrubber further support this conclusion.

Further, the data demonstrate that **PFAS compounds are not volatilized and condensed in the condensate leaving the AquaGreen steam dryer.**

Reference list:

1. Winchell et al, Per- and polyfluoroalkyl substances thermal destruction at water resource recovery facilities: A state of the science review, Water Environment Research, 93: 826–843, 2021
2. Taylor and Yamada, 2003, Laboratory-Scale Thermal Degradation of Perfluoro-Octanyl Sulfonate and Related Precursors
3. Data shown by Casper Schwartz Glottrup, Miljøstyrelsen at Genanvend Biomasse webinar, 2022
4. US EPA Research brief January 2021, Potential PFAS destruction technology: Pyrolysis and gasification
5. EPA PFAS innovative treatment team (PITT) findings on PFAS destruction technologies, EPA Tools & Resources Webinar February 17, 2021, Gullett B.
6. Thoma E. D. et. al., Pyrolysis processing of PFAS-impacted biosolids, a pilot study, Journal of the Air & Waste Management Association, 2022, Vol 72, No. 4, 309-318
7. Thoma E. D. et. al., Pyrolysis processing of PFAS-impacted biosolids, a pilot study, Journal of the Air & Waste Management Association, 2022, Vol 72, No. 4, 309-318, Supplementary material, “SI Table 7. Summary of fluorinated compound canister analysis, acquired at LA”
8. Analytical report no. AR-22-CA-22046613-01, Eurofins Miljø A/S
9. Analytical report no. AR-22-CA-22046651-01, Eurofins Miljø A/S
10. Report no. 228996B-151-122, Eurofins Miljø Luft A/S
11. Report no. 228996A-151-122, Eurofins Miljø Luft A/S
12. Analytical report no. AR-22-CA-22052987-01, Eurofins Miljø A/S
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