

## **Saratoga Biochar Solutions LLC Site Plan Application Supplemental Submission: PFAS Remediation - Technical Information**

**June 6, 2022**

Saratoga Biochar Solution's ("SBS") feedstock treatment process uniquely destroys traces of PFAS, VOCs, pathogens, microplastics, and other contaminants commonly found in biosolids. The SBS Facility is designed to remediate traces of contaminants found in biosolids and shall not accept biosolids with high levels of PFAS contamination or any other hazardous waste. The SBS Facility will be limited to receiving biosolids and unadulterated wood as per the solids waste handling permit.

The SBS Facility helps avoid traces of harmful compounds from being released into the region's air, water and soil from current biosolids disposal methods which do treat PFAS and other contaminants commonly found in biosolids. The SBS Facility will uniquely remediate biosolids while also reducing GHG emissions associated with current biosolids disposal practices.

Contaminants such as PFAS are separated and removed from the solids in SBS's pyrolysis process. After separation, such contaminants exist in a gaseous/oil state commonly referred to as syngas. The syngas is immediately pushed into a multi-staged thermal oxidizer and combusted at 1600-1800 degrees F which is hot enough to break the carbon-fluorine bonds that hold those compounds together, and quickly enough to avoid the elements from reforming other compounds. Thermal oxidation is staged to control nitrogen-based emissions (i.e., N<sub>2</sub>O, NO<sub>2</sub>, etc.) which provides greater thermal control of the thermal oxidation process.

Recent comments made by Moreau and regional residents/stakeholders have indicated a fair amount of confusion about how PFAS will be remediated in the SBS process. Such uninformed comments have shown up in the media, and in statements of concern made directly to Moreau. Here are several examples of this confusion:

- Analogies have been drawn to an organic dairy farm in Maine that experienced PFAS contamination several years ago by directly land applying biosolids that came from a WWTP that had an unusually high level of PFAS in its wastewater which came from an upstream manufacturing facility which used an unusually high level of PFAS in its product manufacturing processes. SBS processes biosolids into Carbon Fertilizer™ specifically to avoid the direct land application of biosolids. There is no direct correlation between the PFAS contamination occurrence in Maine and SBS's process.
- Several PFAS studies have been cited where biosolids were thermally treated at much lower temperatures than SBS will use (i.e., torrefaction), and where there was no follow-on process of thermal oxidation of syngas and advanced air cleaning technologies such as in the SBS treatment process. SBS utilizes a pyrolysis process, not torrefaction. Torrefaction does not reach the time and temperature required to separate the traces of PFAS and other contaminants from biosolids. SBS also utilizes a multi-staged thermal oxidation process to remediate PFAS and other contaminants separated by the pyrolysis process in a way that produces renewable energy to dry the biosolids. There is no direct correlation between such research and SBS's process.

- Several PFAS remediation studies have been cited where the treatment technology involved direct incineration of the solids. Incinerators directly combust biosolids solids to achieve the highest level of PFAS remediation from current biosolids disposal methods. However, incineration doesn't get all the PFAS as PFAS is designed to stick to solids and is less available for destruction. Pyrolysis provides a pathway for separating the PFAS from the solids into a gas where it is more vulnerable for destruction and can be fully remediated. There is no direct correlation between that research and SBS's process.

The attached science and engineering research articles and letters support SBS's assertion that the expected outcome of PFAS remediation is real. Moreover, the NYS DEC verbally set the expectation with SBS during an air facility permit application review call held May 3, 2022, that stack emissions test requirements for permit compliance will contain provisions for residual PFAS testing. Even without such a permit compliance mandate from NYS DEC, SBS commits to stack testing for PFAS as well as mercury and dioxins, regardless. SBS has repeatedly stated that it remediates "the PFAS problem," thus we shall proudly demonstrate our success.

**Attachments:**

1. Letter from Tristan R. Brown, J.D., Ph.D., Director of the Bioeconomy Development Institute, Associate Professor, Department of Sustainable Resources Management, SUNY College of Environmental Science & Forestry, Syracuse, NY
2. Letter from Kathleen Draper, US Director, Ithaca Institute for Carbon Intelligence, Co-Author: "BURN: Using Fire to Cool the Earth" and "Terra Preta: How the World's Most Fertile Soil Can Help Reverse Climate Change and Reduce World Hunger"
3. "Pyrolysis System Effectively Destroys Toxic PFAS"  
Biocarbon Research and Development, CHAR Technologies, Ltd.
4. "Pyrolysis and gasification at water resource recovery facilities: Status of the industry"  
Water Environment Research, February 24, 2022.
5. "Addressing the Impacts of PFAS in Biosolids"  
Water and Wastes Digest, September 10, 2021.
6. "Potential PFAS Destruction Technology: Pyrolysis and Gasification"  
US Environmental Protection Agency, January 2021
7. "Removal of PFASs from biosolids using a semi-pilot scale pyrolysis reactor and the application of biosolids derived biochar for the removal of PFASs from contaminated water"  
Environmental Science Water Research & Technology, Royal Society of Chemistry (Environ. Sci.: Water Res. Technol., 2021, 7, 638)

May 5, 2022

To the Town of Moreau,

My name is Tristan Brown, J.D., Ph.D. I am Director of the Bioeconomy Development Institute and Associate Professor in the Sustainable Resources Management department at the SUNY College of Environmental Science & Forestry in Syracuse, NY. My Ph.D. was in Biorenewable Resources & Technology. I am writing this letter in support of the Saratoga Biochar Solutions project and to provide an important scientific perspective on the project as it relates to PFAS mitigation.

The Saratoga Biochar Solutions project will employ the thermochemical processing pathway pyrolysis to convert biosolids from water resource recovery facilities (WRRF) such as wastewater treatment plants to biochar. Biochar is a solid product this is produced when biomass is decomposed via high temperatures in an oxygen-free environment. The pyrolysis process drives off the biomass's hydrogen and oxygen content to yield carbon-rich biochar. Importantly, pyrolysis is not an incineration process, as combustion cannot occur in the pathway's oxygen-free environment.

The pyrolysis of biomass feedstocks provides multiple critical benefits, including the removal of carbon dioxide from the atmosphere (so long as the biochar produced is not combusted), the building of below-ground carbon (when soils are amended with biochar), and the production of fossil-free fertilizer. These benefits all align closely with the goals that New York has established under the Climate Leadership and Community Protection Act (CLCPA), and biochar is explicitly referred to as an important component of the CLCPA's implementation in the draft Scoping Plan that was released by the Climate Action Council in December 2021.<sup>1</sup>

The Saratoga Biochar Solutions project offers an additional benefit to those listed above in the form of per- and polyfluoroalkyl substance (PFAS) mitigation. These so-called "forever chemicals" accumulate in animals and enter the human food chain, ultimately ending up in human sewage. (PFASs can also be taken up by plants, although natural plant exposure is limited.) The biosolids that are produced by WRRFs are frequently applied to cropland as a fertilizer. While these biosolids are treated to neutralize pathogens, their PFAS content is not normally removed, and cropland that is amended with biosolids in this way can produce food crops that in turn contain PFASs.<sup>2</sup>

The conversion of biosolids to biochar, as the Saratoga Biochar Solutions project will do, greatly reduces the contamination of cropland by PFAS. It does this in two ways. First, the pyrolysis

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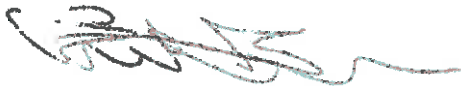
<sup>1</sup> New York State Climate Action Council (2021). "New York State Climate Action Council Draft Scoping Plan," December 30. Available on the Web at: <https://climate.ny.gov/-/media/Project/Climate/Files/Draft-Scoping-Plan.pdf> (accessed May 5, 2022).

<sup>2</sup> Ghisi, R., T. Vamerali, and S. Manzetti (2019). "Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review," *Environmental Research* 169: 326-341, February. Available on the Web at: <https://www.sciencedirect.com/science/article/abs/pii/S0013935118305577> (accessed May 5, 2022).

pathway operates at very high temperatures (up to 1000 degrees Fahrenheit or greater) and destroys the PFASs in the biosolids being pyrolyzed. Recent tests have found up to 96% of the biosolids' PFAS content to be destroyed during the pyrolysis process.<sup>3</sup> Second, whereas biosolids that are applied to cropland are capable of being absorbed by plants, allowing the former's PFAS content to be accumulated in the latter, biochar is inert and strongly resistant to microbial degradation for periods of up to thousands of years,<sup>4</sup> meaning that any PFASs that survive the pyrolysis process will not find their way into the human food chain in the same manner as those from non-pyrolyzed biosolids do.

The Saratoga Biochar Solutions project therefore provides an important human health benefit in addition to its pronounced climate benefits. Biosolids contain PFASs, and those PFASs will continue to enter the human food chain so long as they are landfilled or applied to cropland. By instead destroying and otherwise mitigating the biosolids' PFAS content while converting the biosolids into a safer form of fossil-free fertilizer, the Saratoga Biochar Solutions project will greatly contribute to efforts to prevent the contamination of New York State's food supply by PFASs.

Regards,



Tristan R. Brown, J.D., Ph.D.  
Director of the Bioeconomy Development Institute  
Associate Professor  
Department of Sustainable Resources Management  
SUNY College of Environmental Science & Forestry  
Syracuse, NY  
[Trbro100@esf.edu](mailto:Trbro100@esf.edu)

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<sup>3</sup> Williams, T.O., et al. (2021). "Removal and transformation of PFAS from biosolids in a high temperature pyrolysis system – A bench scale evaluation." *WEF Residuals and Biosolids Conference 2021*.

<sup>4</sup> Rawat, J., J. Saxena, and P. Sanwel (2019). "Biochar: A sustainable approach for improving plant growth and soil properties," in *Biochar – An Imperative Amendment for Soil and the Environment*. Available on the Web at: <https://www.intechopen.com/chapters/65070> (accessed May 5, 2022).



May 11, 2022

To the Town of Moreau:

My name is Kathleen Draper. I have been involved with the biochar industry for over a decade. I am the US Director for the Ithaka Institute for Carbon Intelligence, a non-profit, open-source organization focused on the use of biochar in climate farming and agroforestry, and other industrial uses as well as the Board Chair of the International Biochar Initiative. I frequently write and teach about a wide variety of biochar topics including the use of pyrolysis for sewage sludge. (<https://www.biochar-journal.org/en/ct/81>)

As a longtime advocate of using simple technology to solve complex problems, I am in support of the Saratoga Biochar Solutions project under review in your community. I am aware that Saratoga Biochar will pyrolyze biosolids from wastewater treatment plants to a biochar carbon fertilizer. This is an excellent outcome because the pyrolysis of biomass feedstocks removes carbon dioxide from the atmosphere and, where the biochar product is used as fertilizer or soil amendment, allows for the re-carbonization of agricultural soils.

The Saratoga Biochar project also offers a unique benefit in per- and polyfluoroalkyl substance (PFAS) mitigation. These "forever chemicals" bioaccumulate in animals and to a lesser extent plants and enter the human food chain, ultimately ending up in human sewage. Biosolids are currently and frequently applied to cropland as a fertilizer and although they are pre-treated to neutralize pathogens, their PFAS content (along with other potentially harmful compounds) are not removed.<sup>1</sup>

Saratoga Biochar offer great potential to safely reduce cropland contamination by PFAS and other biosolids undesirable contaminants, as pyrolysis operates at very high temperatures and destroys such compounds in the biosolids being pyrolyzed or separates them into a more vulnerable gaseous state where they are readily destroyed by much higher temperature thermal oxidation. Recent tests have found biosolids' PFAS content is destroyed during the pyrolysis process.<sup>2</sup> Moreover, biosolids that are applied to cropland are capable of being absorbed by plants, allowing their PFAS content to be accumulated in crops. Alternatively, biochar is inert and strongly resistant to microbial degradation for periods of up to thousands of years, meaning that any PFASs that survive the pyrolysis process will not find their way into the human food chain in the same manner as those from non-pyrolyzed biosolids do.<sup>3</sup>

The Saratoga Biochar Solutions project provides an important human health benefit in addition to its very pronounced climate benefits. Biosolids contain PFASs, and those PFASs will continue to enter the human food chain so long as they are applied to cropland. By instead destroying and otherwise mitigating the biosolids' PFAS content while converting the biosolids into a safer form of fossil-free fertilizer, the Saratoga Biochar Solutions project will greatly contribute to efforts to prevent the contamination of New York State's food supply by PFASs.

Sincerely,

A handwritten signature in black ink that reads "Kathleen J. Draper". The signature is written in a cursive, flowing style.

Kathleen Draper

US Director, Ithaka Institute for Carbon Intelligence

Co-Author: "BURN: Using Fire to Cool the Earth" and "Terra Preta: How the World's Most Fertile Soil Can Help Reverse Climate Change and Reduce World Hunger"



1. Ghisi, R., T. Vamerali, and S. Manzetti (2019). "Accumulation of perfluorinated alkyl substances (PFAS) in agricultural plants: A review," *Environmental Research* 169: 326-341, February.
2. Williams, T.O., et al. (2021). "Removal and transformation of PFAS from biosolids in a high temperature pyrolysis system – A bench scale evaluation." WEF Residuals and Biosolids Conference 2021.
3. Rawat, J., J. Saxena, and P. Sanwel (2019). "Biochar: A sustainable approach for improving plant growth and soil properties," in *Biochar – An Imperative Amendment for Soil and the Environment*. Available on the Web at: <https://www.intechopen.com/chapters/65070> (accessed May 5, 2022).



# CHAR Technologies' Pyrolysis System Effectively Destroys Toxic PFAS

By Emma Moreside, EIT, Biocarbon Research and Development

**CHAR**  
technologies

**CHARTECH**  
SOLUTIONS  
**ALTECH**

**Char Technologies Ltd.**  
403 - 789 Don Mills Rd.,  
Toronto, ON, Canada, M3C 1T5  
[www.chartechnologies.com](http://www.chartechnologies.com)





## What are PFAS?

Per- and polyfluoroalkyl substances (PFAS) are a series of manufactured chemicals found in fabrics and materials with non-stick and fire-resistant properties such as carpets, food packaging, Teflon, and fire-fighting foam. When PFAS-containing products are produced and disposed of, PFAS compounds can end up in soils, groundwater, and surface water, where they accumulate and persist as non-biodegradable, toxic compounds. It has been estimated that 95% of the general population have been exposed to PFAS in their lifetime, risking adverse health effects including cancer, liver damage, and immune system disorders [1], [2].

There are more than 4,000 types of PFAS compounds, the most highly produced being perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). These compounds are so damaging that, in 2000, the United States phased out the production of PFOS, and in 2006, eight global companies began phasing out both PFOA and PFOS [1]–[4].



## How do we combat toxic PFAS compounds?

The US Environmental Protection Agency (EPA) has set a lifetime health advisory to a maximum of 70 ppt (parts per trillion) in drinking-water for both PFOA and PFOS combined [1]. There are currently no US EPA regulations for managing PFAS in biosolids, yet there is concern that PFAS from land-applied biosolids can affect surrounding ground and surface-waters. Therefore, in waste materials (e.g., biosolids and sewage sludge/effluents), PFAS compounds must be destroyed before the waste can be safely disposed of. PFAS molecules are structured as a string of carbon (C) and fluorine (F) atoms with attached functional groups of oxygen (O), hydrogen (H), nitrogen (N), sulfur (S), and phosphorus (P). Fluorine compounds are extremely chemically stable, and thus difficult to break down; viable remediation methods must be both effective and economical [1], [2], [4].

PFAS compounds become volatile (can vaporize out of solids) at elevated temperatures (> 600 °C), therefore, high-temperature technologies have been proposed to effectively remove PFAS compounds from waste materials. The most explored destruction technology is high-temperature incineration (> 1000 °C). However, this method is often expensive and introduces other environmental concerns; during combustion, the PFAS carbon-fluorine (C-F) bond is broken, but new compounds of HF, CF<sub>4</sub>, and C<sub>2</sub>F<sub>6</sub> are formed, which are dangerous greenhouse gases [5], [6]. As an alternative to incineration, pyrolysis has been recognized by the US EPA as a promising, cost-effective method of PFAS destruction [7].





## What is pyrolysis?

Pyrolysis is a thermochemical conversion method of upgrading biomass 'wastes' (including PFAS-containing biosolids and sewage sludge) into valuable products of biochar and pyrogas by heating the biomass to elevated temperatures (500 – 850 °C) in an oxygen-free environment (to avoid incineration reactions). Pyrolysis reduces the solids content by up to 90%, making for easier product transport and disposal. Furthermore, the solid biochar product has many value-added applications including soil amendment and carbon sequestration. Pyrogas is produced with biochar, which can be used both to provide heat for the pyrolysis process and upgraded to produce environmentally friendly renewable natural gas (RNG) or green hydrogen (H<sub>2</sub>) (Figure 1).

**Biochar:** Biochar, or 'biocarbon' is the solid component produced during pyrolysis of biomass. It is a flakey, charcoal-like material with a high carbon content. The carbon within biochar is incredibly stable (cannot degrade or release into the atmosphere), making biochar a perfect option for soil amendment and carbon storage.

**Pyrogas:** Pyrogas (also called synethetic gas or 'syngas') is the non-condensable gas produced alongside biochar during pyrolysis. Pyrogas contains hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and other hydrocarbons. Pyrogas has value as an energy source; a portion of the produced pyrogas can be used to internally heat the pyrolysis system, while the remainder can be upgraded into either RNG (>98% CH<sub>4</sub>) or renewable green H<sub>2</sub>



## CHAR's high-temperature pyrolysis system for PFAS elimination

To safely use biochar in land-applications and prevent groundwater leaching, the toxic PFAS compounds must be removed. In the high-temperature, oxygen-free pyrolysis environment, the PFAS compounds are volatilized out of the solids, and are destroyed from the vapour phase through a hydrodefluorination (HDF) pathway during which the C-F bond is converted into a carbon-hydrogen (C-H) bond, where the hydrogen is supplied from the steam-reforming reaction (steam from the moisture in biomass can react with pyrolysis vapours to produce hydrogen) [8].

CHAR Technologies Ltd. (CHAR), in partnership with Western University's Institute for Chemicals and Fuels for Alternative Resources (ICFAR), has demonstrated the destruction of PFAS from biosolids using its high-temperature pyrolysis (HTP) technology. The bench-scale HTP system, which operates as a continuous, mixed bed reactor, processed biosolids from three sites (referred to as Site-1, Site-2, and Site-3) across the US under pyrolysis temperatures of both 500 and 700 °C. Twenty-eight PFAS compounds were targeted for analysis in the inlet (biosolids) and outlet (biochar + pyrogas at Site-3) streams of the system. The total reduction of PFAS from the biosolids was calculated via a mass balance of PFAS-bound F



The biosolids entering the system had on average, a total PFAS concentration of 36 ppm (mg of PFAS compounds/kg biosolids), with PFOS accounting for 50% of the total PFAS-bound F. A summary table of detected PFAS is shown in Table 1. Under 500 °C, PFAS-bound F was eliminated from the solids in Site-1 and reduced by more than 99.3% in Site-2 and Site-3. Even further reduction was achieved at 700 °C, under which PFAS was undetected in Site-1 and Site-3 and reduced by >99.8% in Site-2. PFOS was eliminated from the biosolids at both pyrolysis temperatures.

At 500 °C, although >99% of PFAS-bound F was eliminated, some of that which remained included F in PFOA, which had not been detected in the original biosolids. This could be either because: (1) there was PFOA in the biosolids, but its concentration was not high enough to be detected until the mass reduction in converting biosolids to biochar, or (2) PFAS precursors transformed during pyrolysis to form low concentrations of PFOA, which has been suggested to occur in PFAS-containing water resource recovery facilities (WRRF) [8]. Either way, the higher pyrolysis temperature of 700 °C eliminated 99.8% of PFAS-bound F from the solids, including elimination of PFOA.

For the Site-3 biosolids, the presence of PFAS was also measured in the exiting liquid fraction (condensate and bio oil), and pyrogas to obtain a full picture of the fate of PFAS in all product streams. PFAS-bound F was reduced by a total 84% at 500 °C and 87% at 700 °C from the original biosolids feedstock. The higher temperature evidently had a greater ability to both volatilize and destroy the PFAS compounds. Most of the remaining PFAS existed in the gas phase; 96% and 100% of remaining PFAS-bound F was attributed to pyrogas after pyrolysis at 500 °C and 700 °C, respectively. Understanding how PFAS exists in the pyrogas is crucial to understanding its transformation during pyrolysis but does not pose a high environmental concern; a fraction of the gas will undergo scrubbing treatment and then remain in the pyrolysis system for heat recovery, while the fraction that leaves the system will undergo scrubbing, in addition to either high temperature upgrading (into RNG or hydrogen) or thermal oxidation, each of which will further decompose the gaseous PFAS compounds. In another study, thermal oxidation at 1050 °C eliminated >99.99% of PFAS compounds from the gas phase [9].

After PFAS elimination via pyrolysis, the biosolids, now 'biochar', is considered "Class A Exceptional Quality" under US EPA 40 Code of Federal Regulations (CFR) Part 503.32(a) as they meet quality standards for pathogen reduction and metal limits. The biochar is suitable for land applications including soil amendment, agricultural nutrition, and carbon sequestration [10], [11].

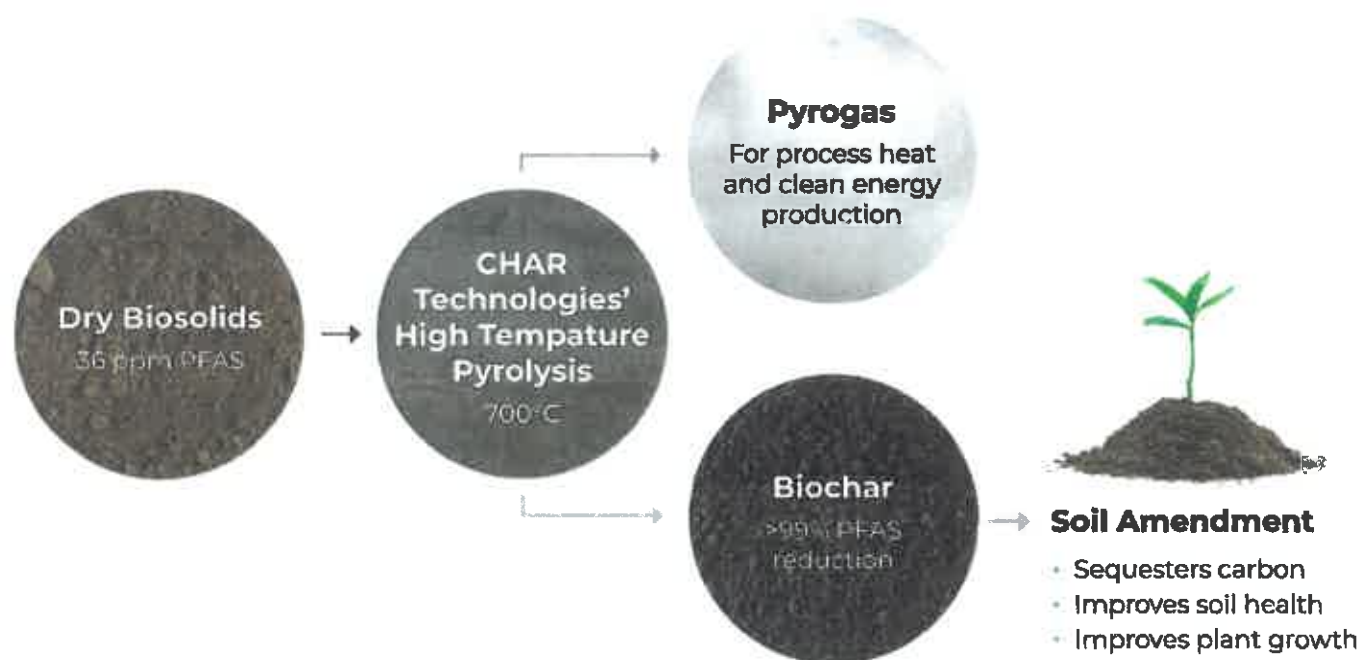


Figure 1: CHAR's HTP system can destroy PFAS from biosolids and produce value-added pyrogas and biochar

## Summary

CHAR has demonstrated PFAS elimination from three biosolids samples using its high-temperature pyrolysis technology; PFAS compounds were eliminated from the solids at >99% after pyrolysis at 700 °C. Further studies will be conducted at CHAR's larger-scale HTP demonstration unit at temperatures up to 800 °C to illustrate the value of a full-scale project in eliminating PFAS from waste feedstocks and creating value-added products.

PFAS Parameter (ppb)	Site 1			Site 2		
	Biosolids	Biochar	Biochar	Biosolids	Biochar	Biochar
	Feedstock	500°C	700°C	Feedstock	500°C	700°C
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	BDL	BDL	BDL	BDL	BDL	BDL
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	BDL	BDL	BDL	BDL	BDL	BDL
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	BDL	BDL	BDL	BDL	BDL	BDL
10:2 Fluorotelomer sulfonic acid (10:2 F)	<b>1.5</b>	BDL	BDL	<b>1.2</b>	BDL	BDL
Perfluorobutane sulfonic acid (PFBS)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorohexane sulfonic acid (PFHxS)	<b>3.8</b>	BDL	BDL	<b>3.6</b>	BDL	BDL
Perfluorotridecanoic acid (PFTrDA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorooctane sulfonic acid (PFOS)	<b>13.7</b>	BDL	BDL	16.6	BDL	BDL
Perfluoropentane sulfonic acid (PFPeS)	BDL	BDL	BDL	BDL	BDL	BDL
N-Et PFO sulfonamide (EtFOSA)	BDL	BDL	BDL	BDL	BDL	BDL
N-Et PFO sulfonamidoethanol (EtFOSE)	<b>6.3</b>	BDL	BDL	<b>4.8</b>	BDL	BDL
N-Et PFO sulfonamidoacetic acid (EtFOSAA)	<b>2.9</b>	BDL	BDL	<b>3.2</b>	BDL	BDL
N-Me PFO sulfonamide (MeFOSA)	BDL	BDL	BDL	BDL	BDL	BDL
N-Me PFO sulfonamidoacetic acid (MeFOSAA)	<b>3.5</b>	BDL	BDL	<b>2.5</b>	BDL	BDL
N-Me PFO sulfonamidoethanol (MeFOSE)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroheptane sulfonic acid (PFHpS)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorooctane sulfonamide (FOSA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorodecane sulfonic acid (PFDS)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorobutanoic acid (PFBA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorodecanoic acid (PFDA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorododecanoic acid (PFDoDA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroheptanoic acid (PFHpA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorohexanoic acid (PFHxA)	<b>1.6</b>	BDL	BDL	<b>1.8</b>	<b>0.26</b>	<b>0.15</b>
Perfluorononanoic acid (PFNA)	<b>1.1</b>	BDL	BDL	BDL	BDL	BDL
Perfluorooctanoic acid (PFOA)	BDL	BDL	BDL	BDL	<b>0.18</b>	BDL
Perfluoropentanoic acid (PFPeA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorotetradecanoic acid (PFTeDA)	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroundecanoic acid (PFUnDA)	<b>1.9</b>	BDL	BDL	BDL	BDL	BDL

\*BDL = Below detectable limit

Table 1: Measured PFAS in biosolids, biochar, and pyrolysis gas after pyrolysis at 500 °C and 700 °C



# Summary

PFAS Parameter (ppb)	Site 3						
	Biosolids Feedstock	Biochar	PyroGas	Biooil	Biochar	PyroGas	Biooil
					500°C		700°C
8:2 Fluorotelomer sulfonic acid (8:2 FTS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	BDL	BDL	<b>0.11</b>	BDL	BDL	<b>0.12</b>	BDL
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
10:2 Fluorotelomer sulfonic acid (10:2 F)	<b>1.2</b>	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorobutane sulfonic acid (PFBS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorohexane sulfonic acid (PFHxS)	BDL	<b>0.45</b>	BDL	BDL	BDL	BDL	BDL
Perfluorotridecanoic acid (PFTrDA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorooctane sulfonic acid (PFOS)	<b>26.6</b>	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoropentane sulfonic acid (PFPeS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
N-Et PFO sulfonamide (EtFOSA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
N-Et PFO sulfonamidoethanol (EtFOSE)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
N-Et PFO sulfonamidoacetic acid (EtFOSAA)	<b>5.3</b>	BDL	BDL	BDL	BDL	BDL	BDL
N-Me PFO sulfonamide (MeFOSA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
N-Me PFO sulfonamidoacetic acid (MeFOSAA)	<b>2.9</b>	BDL	BDL	BDL	BDL	BDL	BDL
N-Me PFO sulfonamidoethanol (MeFOSE)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroheptane sulfonic acid (PFHpS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorooctane sulfonamide (FOSA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorodecane sulfonic acid (PFDS)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorobutanoic acid (PFBA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorododecanoic acid (PFDA)	BDL	BDL	BDL	BDL	BDL	<b>0.042</b>	BDL
Perfluorododecanoic acid (PFDoDA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroheptanoic acid (PFHpA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluorohexanoic acid (PFHxA)	<b>2.2</b>	<b>0.39</b>	<b>19.49</b>	BDL	BDL	<b>1.44</b>	BDL
Perfluorononanoic acid (PFNA)	BDL	BDL	<b>1.68</b>	BDL	BDL	<b>1.21</b>	BDL
Perfluorooctanoic acid (PFOA)	BDL	<b>0.23</b>	<b>2.45</b>	BDL	BDL	<b>0.61</b>	BDL
Perfluoropentanoic acid (PFPeA)	BDL	BDL	<b>4.94</b>	BDL	BDL	<b>1.04</b>	BDL
Perfluorotetradecanoic acid (PFTeDA)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Perfluoroundecanoic acid (PFUnDA)	<b>1.6</b>	BDL	<b>0.47</b>	BDL	BDL	<b>0.281</b>	BDL

\*BDL = Below detectable limit.

Table 1: Measured PFAS in biosolids, biochar, and pyrogas after pyrolysis at 500 °C and 700 °C

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## REVIEW

# Pyrolysis and gasification at water resource recovery facilities: Status of the industry

Lloyd J. Winchell<sup>1</sup>  | John J. Ross<sup>2</sup> | Dominic A. Brose<sup>3</sup>  | Thais B. Pluth<sup>3</sup>  | Xavier Fonoll<sup>4</sup> | John W. Norton Jr<sup>4</sup> | Katherine Y. Bell<sup>5</sup>

<sup>1</sup>Brown and Caldwell, St. Paul, Minnesota, USA

<sup>2</sup>Brown and Caldwell, Troy, Michigan, USA

<sup>3</sup>Metropolitan Water Reclamation District of Greater Chicago, Cicero, Illinois, USA

<sup>4</sup>Great Lakes Water Authority, Detroit, Michigan, USA

<sup>5</sup>Brown and Caldwell, Nashville, Tennessee, USA

## Correspondence

Lloyd J. Winchell, Brown and Caldwell, 370 Wabasha Street North, Suite 500, St. Paul, MN 55102, USA.  
Email: lwinchell@brwncald.com

## Abstract

Wastewater treatment generates solids requiring subsequent processing. Costs and contaminant concerns (e.g., per- and polyfluoroalkyl substances [PFAS]) are challenging widely used landfilling and land application practices. These circumstances are partly driving the re-emergence of pyrolysis and gasification technologies along with beneficial reuse prospects of the char solid residual. Previously, technologies experienced operational challenges leading to revised configurations, such as directly coupling a thermal oxidizer to the reactor to destroy tar forming compounds. This paper provides an overview of pyrolysis and gasification technologies, characteristics of the char product, air emission considerations, and potential fate of PFAS and other pollutants through the systems. Results from a survey of viable suppliers illustrate differences in commercially available options. Additional research is required to validate performance over the long-term operation and confirm contaminant fate, which will help determine whether resurging interest in pyrolysis and gasification warrants widespread adoption.

## Practitioner Points

- Pyrolysis and gasification systems are re-emerging in the wastewater industry.
- Direct coupling of thermal oxidizers and other modifications offered by contemporary systems aim to overcome past failures.
- Process conditions when coupled with a thermal oxidizer will likely destroy most organic contaminants, including PFAS, but requires additional research.
- Three full-scale facilities recently operated, several in construction or design that will provide operating experience for widespread technology adoption consideration.

All the authors are WEF members.

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**KEYWORDS**

air emissions, biochar, char, energy, energy recovery, gasification, PFAS, pyrolysis, residuals, wastewater

**INTRODUCTION**

Wastewater treatment operations generate a solid by-product requiring further processing before beneficial use or disposal. The wastewater industry often refers to the material collected as sewage sludge; however, after further processing to meet federal and state requirements for beneficial reuse, the sludge becomes classified as biosolids (WEF, 2021).

In 2019, the United States Environmental Protection Agency (USEPA) estimated that 4.75 million dry tonnes of “biosolids” were produced in the United States (US) (USEPA, 2021a) by water resource recovery facilities (WRRF), processing over 3.8 megaliters per day. Roughly 51% of “biosolids” in the US were land applied to recycle the nutrient content and enhance soils. Other practices included reuse or disposal in landfills (22%), incineration (16%), and the remaining 11% using surface disposal sites or other management practices.

Shifts in acceptable land-use practices, regulations, and public concern for unregulated chemicals have disrupted historical sludge and biosolids applications in the US. For example, increasing population density, regulations, and general aversion to reuse of human waste products have strained the acceptance of sludge or biosolids land application practices (Collins, 2019; Slaughter, 2013). Similarly, a reduction in number (USEPA, 1994) and difficulty in permitting new landfills has led to recent increases in landfill tipping fees in more populated regions of the US (EREF, 2021). In addition, increasing public interest in per- and polyfluoroalkyl substances (PFAS) and emerging pollutants has further complicated traditional sludge and biosolids practices (Boxall et al., 2012; Kinney et al., 2006; Navarro et al., 2018; Sepulvado et al., 2011; Walters et al., 2010; Winchell et al., 2022), forcing many municipalities to reconsider end uses.

Pyrolysis and gasification systems are emerging in the wastewater market as thermal treatment processes that could significantly reduce the mass of sludge or biosolids, reducing requirements for off-site transportation and provide a means for removing or destroying, considered the complete defluorination regardless of carbon oxidation extent, PFAS and other emerging pollutants (Horst et al., 2020; Patel et al., 2020; USEPA, 2021c; Winchell, Ross, et al., 2021). Pyrolysis processes sludge or biosolids in the absence of oxygen, typically at high temperatures

(Winchell, Ross, et al., 2021). Gasification is similar but includes substoichiometric oxygen levels and operates at higher temperatures than pyrolysis (Winchell, Ross, et al., 2021). During pyrolysis, sludge or biosolids undergo thermochemical conversion into products representing all three phases—gas, liquid (aqueous or non-aqueous), and solid (char) (Liu et al., 2017). If controlled streams of a gasifying medium (e.g., air, oxygen, or steam) are introduced into the process, the pyrolysis products will be further refined into a lighter-molecular weight, non-condensable off-gas, also called product gas or syngas (Basu, 2013). The off-gas can be combusted on-site or transferred to remote users as an energy source (Basu, 2013; Han et al., 2019) and as a cleaning step prior to releasing the subsequent “flue gas” after the oxidation process to the environment (USEPA, 2021c). Pyrolysis and gasification processing trains show promise for wastewater utilities because PFAS and other emerging pollutants may be removed, and in some cases destroyed, through these high-temperature processes (USEPA, 2021b; Winchell, Ross, et al., 2021). Still, the efficiency has yet to be documented (Winchell, Ross, et al., 2021). This potential benefit, coupled with the reduction in mass requiring subsequent handling, has driven interest in pyrolysis and gasification as an alternative to historically proven incineration systems (Patel et al., 2020; USEPA, 2021b, 2021c).

This paper provides a current description of pyrolysis and gasification technologies, focusing on US applications. An overview is provided that summarizes the historical challenges for full-scale implementation and recent advancements in technology deployment. The documented fate of various unregulated chemicals, primarily PFAS, is compiled, and gaps in current understanding are identified through these process trains. This information offers professionals working in the wastewater industry an objective introduction to these technologies for potential applications.

**PYROLYSIS AND GASIFICATION OVERVIEW**

Pyrolysis and gasification have long garnered interest for their ability to convert difficult-to-handle organic feedstocks into gaseous or liquid fuels that can more easily be stored and used in conventional combustion applications

(Bridle & Skrypski-Mantele, 2004; Haug & Lewis, 2014; Kroll et al., 1983). Additionally, these techniques can process the solid phase material into a carbon-rich product, called char or biochar, with unique and valuable properties for agricultural and industrial applications (Callegari & Capodaglio, 2018). For example, coal has been gasified since the 18th century, when it was used to produce town gas for street lighting and is still gasified today to produce raw materials for chemical manufacturing (Basu, 2013). Pyrolysis is also used at commercial scale to generate chemical feedstocks, renewable fuel oil, and commercial char soil amendments from various feedstocks, including woody biomass, agricultural residue, and energy crops (Han et al., 2019).

Pyrolysis and gasification have also received strong interest as a thermochemical treatment alternative to incineration (Liu et al., 2020; Safferman et al., 2017; USDOE, 1997; USEPA, 1985). While these technologies can achieve mass reduction comparable to incineration, they require less combustion air and consequently produce less flue gas needing treatment (Winchell et al., In Review). Further, pyrolysis and gasification allow for intermediate treatment, or conditioning, of the off-gas to remove or recover particulates and acid gases before energy-producing combustion processes (Asadullah, 2014).

## Thermal reactions

Numerous thermal reactions are involved with pyrolysis, gasification, and combustion, and a high-level overview of these reactions is presented here. For a more detailed treatment, the reader is directed toward Basu (2013), Boateng (2020), and Higman and van der Burgt (2008) for reviews of the process fundamentals of biomass pyrolysis and gasification.

## Pyrolysis

When considered as a standalone process, pyrolysis is the thermochemical decomposition of an organic feedstock into a carbon-rich char and a hydrocarbon-rich off-gas. A portion of the off-gas can be condensed into non-aqueous (oil or tar) and aqueous phase liquids. Pyrolysis is a prerequisite step to generate the combustible char and off-gas products from solid or heavy liquid fuels for subsequent oxidation (partial or complete) in gasification or combustion processes (Basu, 2013). The process is conducted in the total, or near-total, absence of air or oxygen, typically at temperatures between 300°C and 850°C, with the lower end of the range representing the

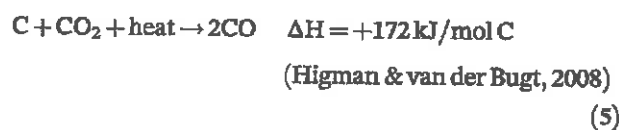
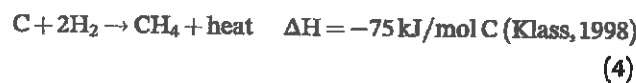
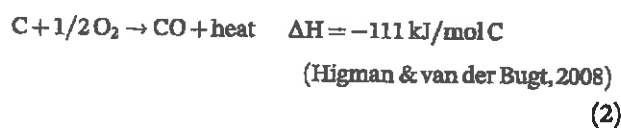
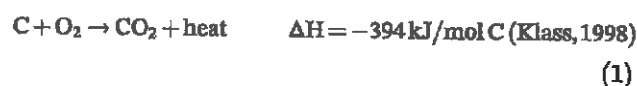
transition from torrefaction (Basu, 2013; Bridle & Pritchard, 2004). The off-gas contains a diverse mixture of compounds, including hydrogen ( $H_2$ ), methane ( $CH_4$ ), carbon monoxide (CO), carbon dioxide ( $CO_2$ ), acetylene ( $C_2H_2$ ), ethylene ( $C_2H_4$ ), ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ), benzene ( $C_6H_6$ ), and others (Basu, 2013; Liu et al., 2017). The yield of the different products depends on several factors, including feedstock heating rate, catalysts, maximum temperature (or pyrolysis temperature), and residence time and heat distribution in the reactor (Boateng, 2020). The heating rate is often used to distinguish broad categories of pyrolysis (Basu, 2013). Slow pyrolysis is the term used to characterize systems operating at lower heating rates (with corresponding vapor residence times on the order of minutes) which favors char production (Basu, 2013; Boateng, 2020). In fast pyrolysis, residence times are on the order of seconds. In addition to primary feedstock decomposition, secondary decomposition, or “cracking” of the larger molecular weight condensable gases into lighter non-condensable gas, can occur with extended vapor residence times and higher temperatures (Gao et al., 2014; Han et al., 2019). Secondary cracking can be promoted via the reaction of vapors with heated char, sludge ash, or metallic catalysts (Liu et al., 2022, 2021). Pyrolysis produces a range of products influenced by these environmental conditions including all three material phases—solids, liquids, and gases. Numerous review papers have documented the yield distribution of sludge or biosolids pyrolysis products at various processing parameters with the overall trend being that as pyrolysis temperature increases, the biochar yield (typically between 30% and 50%) decreases with a corresponding increase in gas production (Chen et al., 2014; Gao et al., 2014; Hossain et al., 2011; Jin et al., 2016; Lu et al., 2013; Paz-Ferreiro et al., 2018; Song et al., 2014; Yuan et al., 2015). The pyrolysis energy reactions will depend on the processing conditions and type of biosolids (Hossain et al., 2009) but often result in a net energy requirement (Daugaard & Brown, 2003; McNamara et al., 2016). As such, the process typically requires supplemental energy for feedstock heating, vaporization of moisture from the feedstock, and reactor radiant heat loss (Ponsa et al., 2017).

## Gasification

Gasification advances thermochemical transformations beyond those in pyrolysis by reacting char and volatile vapors with a gasifying medium (such as air, oxygen [ $O_2$ ], or steam [ $H_2O$ ]). Gasification refines gaseous products of pyrolysis into a lower molecular weight fuel. Specifically, the full and partial oxidation of pyrolysis



products yields CO and CO<sub>2</sub>, which are then reacted with steam, elemental hydrogen, and carbon (C) in a final reductive (or gasification) zone to generate an off-gas consisting mainly of CO, H<sub>2</sub>, and CH<sub>4</sub> (Ahmad et al., 2016; Oladejo et al., 2019). The gasifying medium feed rate and reactor operating temperature control the extent of oxidation, heat release, and limits ash agglomeration and heat production to support endothermic reactions, reactor radiation losses, and latent and sensible heat demands to maintain reactor temperatures at approximately 800–1,000°C (Ahmad et al., 2016; Basu, 2013). A summary of some of the primary reactions within a gasifier is provided (Reactions 1–5) (repurposed from Basu, 2013).



## Contemporary systems

Contemporary pyrolysis and gasification systems treating sludge or biosolids must address operational issues associated with systems from the past. Today, active installations have addressed historical shortcomings by simplifying the process, repurposing demonstrated technology components, and improving system controls per the following discussion.

### Historical lessons

Sludge and biosolids pyrolysis and gasification systems in operation or under development today in the US

represent the evolution of the technology from its initial application in the early 1970s. To the authors' knowledge, the first commercial-scale use of pyrolysis or gasification with sludge was deployed at the Central Contra Costa Sanitary District (Brown and Caldwell, 1976) when the WRRF's two multiple hearth furnaces were run in oxygen-deficient conditions during facility startup in 1975. Later, two 36-dry tonnes per day (dtpd) multiple hearth furnaces were installed at the Arlington County, Virginia Advanced Water Treatment (AWT) Facility in 1983 capable of incinerating or gasifying sludge by limiting combustion air input and oxidizing the off-gas in an afterburner with waste heat recovery (Kroll et al., 1983). Full-scale operation of these furnaces demonstrated that gasification of sludge was possible. However, both WRRFS ultimately operated the systems in incineration mode due to the additional complexity and cost of maintaining the afterburner and heat recovery systems.

In a similar timeframe, the city of Los Angeles constructed an extensive sludge gasification system with three trains, each with a capacity of 120 dtpd. The system was noted to have operated for 10 years until being decommissioned due to difficulties with the Carver-Greenfield drying process and other considerations (Haug & Lewis, 2014).

Several lessons learned at a pyrolysis plant in Australia were identified (Bridle & Skrypski-Mantele, 2004). First, the upstream solids processing performance must be verified as the sludge quality variability required a capital upgrade of the dryer process. Operators of the pyrolysis system benefit from an industrial background to reliably manage the system, including all related processes. Tubes in the off-gas condensing equipment fouled and were replaced with a direct spray system. Regardless, the downstream oil-water separator still required monthly cleaning. The authors noted other issues with char handling and emergency venting that required ancillary equipment modifications and replacement.

A more recent gasification example includes the 160 wet tonnes per day (wtpd) system at the city of Sanford, Florida; the facility, owned by Maxwest Environmental Systems, Inc., was operated from 2009 to 2014 (Snyder, 2015). While initial operational issues required costly modifications that ultimately led to the facility's closure, the modifications did result in a technology configuration that achieved stable operations, albeit for a limited time. Specifically, the dryer and dried product delivery system were changed from batch to continuous feed to stabilize process loading and off-gas production. The gasifier reactor was also changed from a fixed bed updraft configuration to a fluidized bed to improve heat transfer and temperature control. Discussion with a

technology provider familiar with the facility's operation also identified system shutdown as an additional challenge (McGolden, 2021). The unit had to be shut down with product retained inside to protect the uninsulated steel floor from exposure to high temperatures. This resulted in air intrusion and "burn out" of the product, reaching high temperatures that would melt the resulting ash into slag that required chipping out before starting up again.

KORE Infrastructure completed a 6-year demonstration test of biosolids pyrolysis in 2014 at the Los Angeles County Sanitation District's Joint Water Pollution Control Plant in Carson, California. The project's primary finding was that system maintenance and rehabilitation requirements during operation were primarily associated with hydrogen sulfide corrosion from the pyrolysis off-gas (Wirtel, 2021). High levels of hydrogen sulfide were observed in the pyrolysis off-gas and KORE Infrastructure noted that their plans for future, permanent installations will include a detailed pyrolysis off-gas characterization and materials selection assessment to address hydrogen sulfide corrosion potential.

Logan City Council (2021) in Queensland, Australia, recently conducted a biosolids gasification demonstration project at the Loganholme Wastewater Treatment Plant between January and August 2020. During the project, 12 test runs of a multiple hearth gasifier manufactured by Pyrocal Pty Ltd. were operated at a dried-biosolids feed rate of 480 kg/h (74% of maximum capacity at 650 kg/h). Over the longer duration runs (100 h), system throughput was reduced due to soot and tar build-up in the air manifolds. However, the soot and tar readily burned off when the feed was paused, and an automated burn-off sequence is planned for future operation at full scale. Additionally, the pyrolysis off-gas' non-sticky carbon and dust carryover overwhelmed the original spray absorber scrubber and barrier filter located after the directly coupled thermal oxidizer. As a result, the system was modified to include a Venturi device at the front of the scrubber instead of the barrier filter. In addition, a wet electrostatic precipitator (WESP) is planned for inclusion at full scale for improved dust control.

Newer generation pyrolysis and gasification systems have incorporated these lessons learned into their design and operation by improving construction materials, simplifying design of energy recovery systems (i.e., using air and hot water mediums in lieu of thermal oil or steam), and integrating demonstrated technology components (i.e., dust control and product feeding subsystems) with modern instrumentation and controls to improve reliability (McGolden, 2021; Mooney, 2021; Villa, 2021). While substantial progress has been made in these systems, further evidence of successful operation over the long term

is required before they can be considered proven at commercial scale.

## Active installations

As discussed previously, application of sewage sludge or biosolids pyrolysis and gasification has been limited so far in the US. At the time of writing, the authors identified three commercial-scale facilities in operation processing sludge in the US (Table 1).

All the systems noted in Table 1 consist of three core unit processes, schematically represented in Figure 1. The first process dries the sludge or biosolids to the desired moisture content. The system then processes the dried product through the thermal reactor where pyrolysis and, if intended, gasification occur. Finally, the off-gas from the thermal reactor is combusted in a thermal oxidizer for energy recovery and air emissions control. Sub-unit processes include product feeding, residual char handling from the thermal reactor, and energy recovery systems. The following discussion and later technology comparison section discuss these processes in more detail.

## Moisture reduction

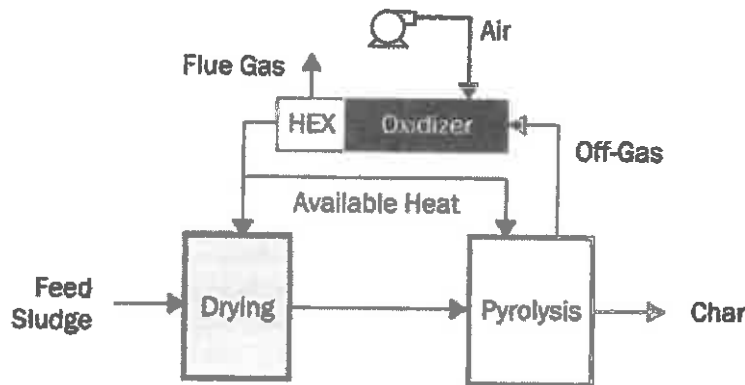
The existing facilities demonstrate two approaches to reducing moisture—a critical preparation step in sludge or biosolids pyrolysis or gasification. The Ecoremedy and Bioforcetech facilities use a discreet upfront drying step. The Ecoremedy technology uses a single-pass rotary drum dryer to produce a dried pellet meeting Class A requirements under the USEPA biosolids regulations 40 C.F.R. § 503 (Ecoremedy, 2021; USEPA, 1993). The Bioforcetech pyrolysis facility uses batch-fed biodryers to reduce moisture content through heating, applied via an initial, exothermic composting step, and subsequently from an auxiliary hot water system (BioForceTech Corporation, 2022). The Aries Clean Technologies gasification facility takes a different approach by using wood waste and scrap tire feedstocks as bulking agents to reduce the moisture content of the blended feed, which allows for the recovery of additional energy from the gasification of the bulking agents (Rulseh, 2018). Traditionally, thermal drying can be a costly, complex, and energy-intensive process (WEF, 2018), and the use of bulking agents represents an opportunity to eliminate this step. However, feedstock blending with a downdraft gasifier limits biosolids content to approximately 10% of the blended feedstock mass, which requires ongoing coordination with third-party suppliers (Rulseh, 2018).

**TABLE 1** Commercial pyrolysis and gasification facilities currently processing sludge in the United States

Location	Technology vendor	Commissioned	Rated capacity	Maximum energy production	Reported mass output
Morrisville Municipal Authority, Pennsylvania <sup>a</sup>	Ecoremedy Fluid Lift Gasification™ (Ecoremedy, 2021)	2019	32 wtpd (27% total solids)	2640 MJ/h heat in process air for thermal drying	2.4 wtpd
Silicon Valley Clean Water Authority, California	BioForceTech Corporation BioDryer and Pyrolysis (BioForceTech Corporation, 2022)	2018	14 wtpd of dewatered, digested biosolids (20% total solids)	320 MJ/h heat in hot water for drying	1.1 wtpd
City of Lebanon, Tennessee	Aries Clean Technologies Downdraft Gasification (Rulsch, 2018)	2016	29 wtpd of blended waste wood, scrap tires, and dewatered, digested biosolids	420 kW of electricity from flue gas driven organic Rankine cycle generator	1.5 wtpd

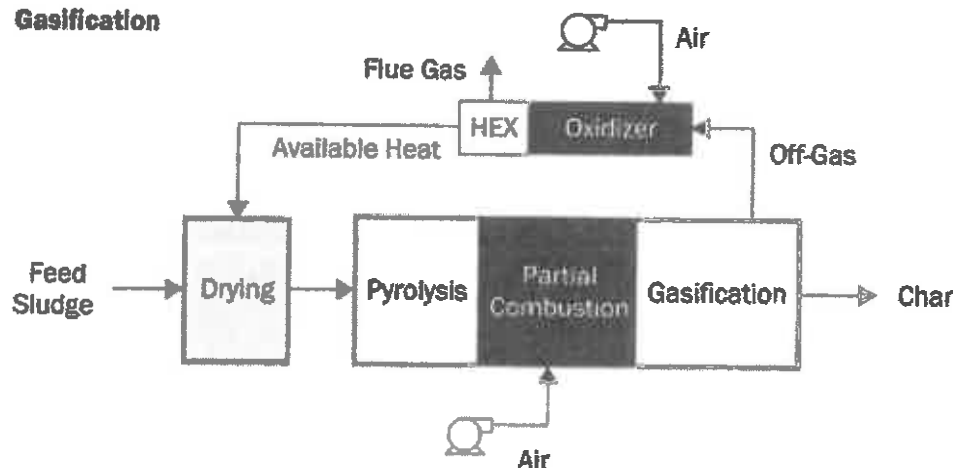
<sup>a</sup>System demonstration recently completed, and equipment decommissioned.

## Pyrolysis



**FIGURE 1** Pyrolysis and gasification process schematics illustrating the various sub-processes and differentiating use of a gasifying medium, air for this example

## Gasification



Each of these facilities processes a sludge that has undergone aerobic or anaerobic biological treatment before drying. Minimizing or eliminating upstream stabilization presents an opportunity to increase the energy density of the feed sludge, especially for feedstocks containing primary sludge from wastewater treatment. However, stabilization provides equalization in flow and loading to thermal drying processes. In addition, it safeguards the system from high levels of odors, internal product adhesion, and reactor fouling, which have been associated with dryer operations with unprocessed primary sludge (WEF, 2018). Consequently, advancements in drying technology and system design will be required to reliably apply pyrolysis and gasification to unstabilized sludge.

## Thermal reactor

A variety of thermal reactor types exist for pyrolysis and gasification. A brief description of reactor types applied to wastewater sludge and biosolids at a commercial scale is provided here. The reader is referred to Gao et al. (2020), Patel et al. (2020), and Basu (2013) for a more comprehensive discussion of reactor types and processing parameters. Landen (2018) completed a survey of approximately 200 biomass pyrolysis and gasification manufacturers worldwide and identified four primary reactor types used by manufacturers operating at least five systems at commercial scale (10,000 tonnes capacity per year) globally. A summary of the findings, updated with more recent technology installations, is provided here.

Landen (2018) identified three reactor concepts for biomass pyrolysis relevant to sludge or biosolids: a heated reactor with an auger, a reactor with a heated auger, and a rotary kiln. The study also identified multiple reference installations of batch kiln reactors used to produce charcoal from wood biomass; however, the batch process included a high operational and footprint demand that can be prohibitive for WRRFs.

The heated reactor with auger, as manufactured by PYREG GmbH and packaged by BioForceTech Corporation, uses a double-wall reactor where hot exhaust from direct combustion of the pyrolysis off-gas is passed through the outer chamber to heat the wall of the inner chamber (BioForceTech Corporation, 2021). The feedstock is transferred along the inner chamber via a shafted screw auger and absorbs heat from the wall while undergoing pyrolysis. KORE Infrastructure manufactures a pyrolysis system with a similar concept, where two horizontal augered reactors are operated in series inside a chamber heated externally with hot flue gas from the pyrolysis off-gas burner (Kore Infrastructure, 2021).

Feedstock characteristics are required to be kept within a specific operating range to absorb heat evenly along reactor walls to guard against material stress and ash agglomeration from localized hot spots.

ETIA Ecotechnologies alternatively uses an electrically heated, shaftless screw auger to convey and heat biomass along an insulated reactor, improving the system's capacity for temperature control but eliminating the ability to meet process heat demands by direct combustion of the pyrolysis off-gas (ETIA Ecotechnologies, 2021).

The third reactor type transfers biomass along an externally rotated kiln with an external heating chamber. CHAR Technologies Ltd. is one representative manufacturer of this rotary kiln pyrolysis system that uses multiple pyrolysis off-gas burners to provide process heat at controlled rates to the heating chamber and requires off-gas cleaning prior to combustion in the burner system, creating the potential for tar condensation and associated reduction in heating value of the off-gas (CHAR Technologies, 2021). However, the rotary kiln eliminates the need for moving parts in the hot zone of the reactor and the associated concern for material stress and wear.

Green Waste Energy employs a different technology using a tower reactor that introduces the feedstock at the top, which falls and undergoes pyrolysis treatment (Green Waste Energy, 2021). Treated off-gas recycles to burners installed on the tower jacket to satisfy heat requirements. Landen (2018) established that a critical feature of all pyrolysis reactor types is their ability to minimize or eliminate contact between pyrolysis off-gases and biochar to preserve characteristics of the latter.

In contrast to the indirectly heated pyrolysis reactor systems described above, gasification derives its process heat from the limited combustion reactions conducted within the reactor. Consequently, gasification systems are less dependent on reactor surface area, a feature that Landen (2018) identified as a limiting factor for scaling up pyrolysis reactors.

The introductory location of the combustion air, or gasifying medium, is critical for heat distribution within the reactor and is a primary differentiator between gasifier reactor configurations (Basu, 2013). The feedstock and gasifying medium enter the reactor from opposite ends in updraft gasifiers. The pyrolysis process is allowed to advance to separate off-gas from char, which then contacts with combustion air. As the oxygen is depleted, the gas moves toward the feedstock entrance, transferring sensible heat and undergoing reductive, gasification reactions.

Landen (2018) identified the moving grate gasifier, manufactured by Ecoremedy LLC, as a promising reactor type, in which combustion air is injected beneath a grate

used to advance biomass through the process. The air is injected in several zones, each of which can be modeled as individual updraft gasifiers to control system temperature and char oxidation.

The gasifier manufactured by Pyrocal Pty Ltd. uses a multiple hearth reactor that transfers biomass by rotating rake arms and introduces combustion air in the final zone where the hot gases pass up through the reactor (Logan City Council, 2021). In downdraft gasifiers, the feedstock and oxidizing medium are introduced at the reactor entrance to promote immediate contact with pyrolysis off-gas, promoting pyrolysis off-gas cracking and tar reduction.

A similar concept is employed in fluidized bed reactors where the air and feedstock are reacted together in an inert fluidized bed to promote mixing and heat transfer. The design subjects the gas stream to gasification reactions as it travels toward reactor zones where the oxygen has been consumed. The fluidized bed reactor allows for operation at larger scale, as evidenced by the current development of two large fluidized bed gasification facilities by Aries Clean Technology in urban centers in the US (Aries Clean Technologies, 2021).

## Energy recovery

Energy recovery is currently employed in pyrolysis and gasification facilities that process waste streams. The energy recovery step is typically achieved through onsite, direct-combustion of the off-gas instead of processing it for use off-site chemical or fuel production. Product conditioning to produce an off-site chemical or fuel (most commonly a bio-oil from pyrolysis and syngas from gasification) is a highly complex field of study. Specialized knowledge is required to design and operate these systems (Han et al., 2019).

One concern of pyrolysis and gasification is the resulting condensable fraction (aqueous or non-aqueous) of the off-gas, commonly referred to as tar, that forms as a liquid in low-temperature zones of a reactor and downstream gas handling equipment (Ponsa et al., 2017). Tar is a viscous liquid that can plug downstream passages and energy conversion equipment, including gas engines (Basu, 2013). Tar production can be minimized through reactor design and off-gas cleaning; however, off-gas cleaning processes impart an operational and parasitic energy demand which can result in difficult to treat waste streams (Basu, 2013).

Alternatively, tar production can be induced under controlled conditions for energy recovery (Gao et al., 2020; Haghghat et al., 2020; Hossain et al., 2009; Kim & Parker, 2008). However, handling of the liquid

material introduces unique challenges. The higher oxygen content in biomass feedstocks compared to fossil fuels results in a bio-oil product that is less energy-dense, potentially unstable in combustion applications, corrosive, and increasingly viscous over time (Basu, 2013).

Thermal oxidizers (direct combustion) employed at the three existing, commercial-scale facilities combust raw off-gas from pyrolysis or gasification directly before tar has a chance to form (BioForceTech Corporation, 2022; Ecoremedy, 2021; Rulseh, 2018). Thermal oxidizers mitigate operation risks and convert all the chemical energy stored in the condensable and non-condensable fractions of the off-gas (Niessen, 2002). The heat from thermal oxidation can be transferred through heat exchangers to process air, hot water, steam, or drive an organic Rankine cycle (ORC) generator, which is used at the Aries Clean Technologies facility. A schematic of the sequential processes occurring with pyrolysis and gasification followed by direct combustion is provided in Figure 1.

The defining question for the energy balance of each system is whether the available heat recovered from combustion is sufficient to meet the demands for upfront drying and internal heat sinks. As conventional thermal drying has historically required a large amount of fuel, drying with pyrolysis and gasification requires a relatively high level of conversion efficiency to achieve autothermal operation (WEF, 2018).

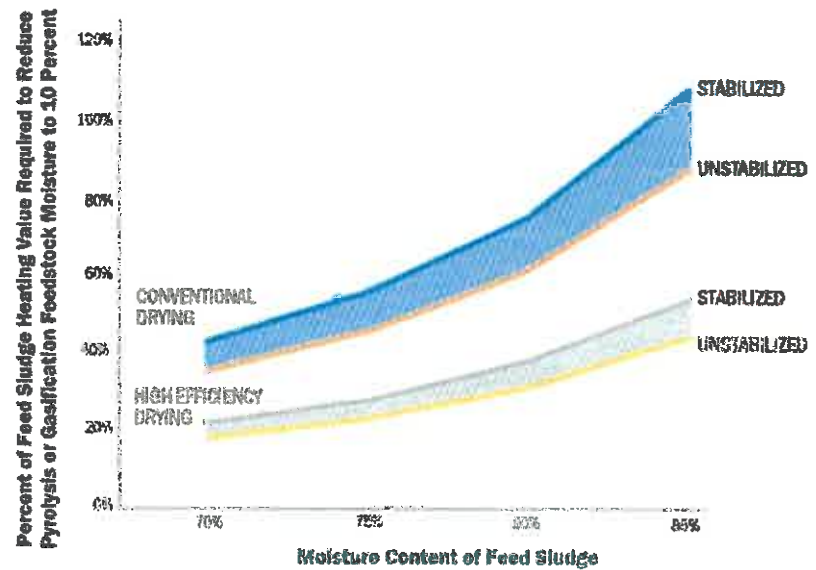
A conceptual relationship between the efficiencies required for converting chemical energy in sludge or biosolids to meet the heat demands of conventional and developing high-efficiency dryer technologies (e.g., biodryers) is presented in Figure 2. While unreacted carbon in char limits recoverable heat, as well as various other heat sinks, direct combustion of pyrolysis and gasification off-gases, theoretically, can exceed the heat needed for drying; however, the net impact has not yet been quantified, as operational data from full-scale facilities are not yet publicly available. Future work is required to assess operational data to measure and verify critical process variables and energy performance indicators, such as percent available heat recovery from feedstock, to verify successful operation.

## Operating conditions

Given that these technologies are emerging in the wastewater marketplace, several equipment suppliers were surveyed to document operating conditions. Table 2 summarizes the information collected based on the dewatered solids characteristics footnoted. The unit feed rate ranged broadly with capacities capable of handling solids output from most WRRFs with a single train.



**FIGURE 2** Net percent heat recovery from feed sludge chemical energy required to reduce pyrolysis or gasification feedstock moisture to 10%. Assumes (a) thermal efficiencies for conventional and developing high-efficiency dryers of 3.0 and 1.5 kJ-heat/g-water, respectively (BioForceTech Corporation, 2022; WEF, 2018); (b) input sludge higher heating value of 23.8 kJ/g-volatile solid (Niessen, 2002); and (c) volatile solid contents of 65% and 80% for stabilized and unstabilized sludge, respectively (WEF, 2018)



Dryer operation varied the most between vendors compared to the other unit processes. Solids residence time in the dryers reflected the operating temperatures (i.e., increasing time with lower temperature). Supplier 2 differed the most from others based on the biologically driven heating concept resulting in the highest energy efficiency but the longest solids residence time. Overall, dryers required the bulk of the energy recycled in the process.

Thermal reactor operation values were more consistent across the suppliers surveyed. Target operating temperatures ranged over 300°C, but vendors noted the value must be modified depending on the off-gas and char production goals. Gas residence times also appeared supplier-tailored and not technology-dependent as some operated at approximately 1 s while others approached 10 s. Suppliers reported similar solids residence times except Supplier 1, which processed up to six times longer. Pyrolysis systems did require recycled energy to maintain operating temperatures where the gasifiers used the heat released from internal partial combustion.

Each supplier provided the thermal oxidizer to destroy pollutants and liberate heat from the hydrocarbon-rich off-gas combustion. The suppliers operated at similar temperatures and residence times, except Supplier 1 exceeded the temperature range provided by the others. This high temperature is conceivable given the relatively low stoichiometric air requirement, which acts as a heat sink.

The resulting char characteristics in Table 2 are an example only. Each supplier can change their process to shift the char to either more or less carbon-rich depending on the site-specific goals. For example, Supplier 1 typically converts the feedstock to ash compared

to Supplier 2 who intentionally produces a char product with high carbon content. A higher carbon char reduces the amount of heat released during the thermal conversion and can lead to supplemental fuel requirements but provides a potential means for long-term carbon sequestration in the char product (Callegari & Capodaglio, 2018; Patel et al., 2020; Racek et al., 2020). Alternatively, a lower carbon char reduces the mass of residual product needing to be managed.

## Char

During pyrolysis and gasification, off-gas production increases as temperatures increase, while char yields decrease (Song et al., 2014; Yuan et al., 2015). Sludge- and biosolids-derived char have been widely studied for their beneficial reuse potential, primarily as soil amendments for turfgrass and agricultural crop applications (Callegari & Capodaglio, 2018). Char is a beneficial soil amendment; however, properties important to soil quality, such as pH, cation exchange capacity, and nutrients, can vary widely and are dependent on feedstock and pyrolysis temperatures (Al-Wabel et al., 2018). Additionally, while char can be described as a material derived from sludge or biosolids, as defined in USEPA's biosolids regulations 40 C.F.R. §503 (USEPA, 1993), it may be a lengthy process for producers to receive recognition of char as an Exceptional Quality or Class A biosolids product from regulators and use it as a soil amendment.

Char from a range of feedstocks, including sludge and biosolids, has been shown to have a liming effect on soils, improve water holding capacity, and increase crop

TABLE 2 Thermal treatment operating conditions<sup>a</sup>

Parameter	Units	Supplier 1	Supplier 2	Supplier 3	Supplier 4	Supplier 5
<b>Process</b>						
Unit feed rate range	Dry tonne/d	6.1–24.4	2.1–6.8	22–110	22–90	6.7–56.7
<b>Dryer</b>						
Type	–	Rotary drum	Rotary cylinder	Belt in tandem with rotary drum	Rotary drum	Rotary drum
Target total solids	Percent	92	80	90	90	60
Temperature	°C	535 inlet 100 outlet	65	80–105	510 inlet 87 outlet	800 inlet 110 outlet
Solids residence time	min	15	3,330	220	20	20
Evaporative capacity	kg H <sub>2</sub> O/h	2,720	720	14,500	13,600	4,960
Thermal efficiency	kJ/kg of H <sub>2</sub> O	3,400	1,939	N/P	2,775	2,685
Supplementary fuel	kJ/h per dry tonne/d	0	0	0	0	45,100
Recycled energy input <sup>b,c</sup>	kJ/h per dry tonne/d	281,100	296,000	N/P	416,200	168,000
<b>Reactor</b>						
Type	–	Moving chain grate	Inclined screw	Passive falling tower	Fluidized bed	Rotary kiln
Temperature	°C	750	620	950	680	650–850
Gas residence time	s	1	7–8.5	10	8–10	1.2
Solids residence time	min	90	15	15	20	20
Stoichiometric air	–	0.3	0.0	0.0	0.32	0.0
Supplementary fuel	kJ/h	0	0	0	0	0
Recycled energy input <sup>b,c</sup>	kJ/h per dry tonne/d	0	76,300	N/P	0	190,400
<b>Thermal oxidizer</b>						
Type	–	Proprietary	Flameless direct fired	Regenerative thermal oxidizer	Direct fired	Staged air cyclone
Temperature	°C	1,200	980	850	980	850
Gas residence time	s	2	2.5–3.5	2.5	1–2	2
Flue gas flow rate <sup>b</sup>	Nm <sup>3</sup> /h per dry tonne/d	300	180	N/P	400	330
Supplementary fuel <sup>b,d</sup>	kJ/h per dry tonne/d	0	0	0	0	2,400
Stoichiometric air	–	1.15	1.15	N/P	2.9	N/P

TABLE 2 (Continued)

Parameter	Units	Supplier 1	Supplier 2	Supplier 3	Supplier 4	Supplier 5
Process		Gasification	Pyrolysis	Pyrolysis	Gasification	Pyrolysis
Energy recovered <sup>e</sup>	Percent of available from flue gas sensible heat	79	71	70 <sup>f</sup>	75	65 <sup>g</sup>
Major motor requirements <sup>b</sup>	KW/dry tonne/d	4.7	23.5	1.8	15.7	4.0
Solid residual						
Production	Percent of dry feed	25	45	N/P	27	35.8
Combustible fraction	Percent	0	10	N/P	14	16-30
Carbon content	Percent	0	30	<2	14	15-25
Nitrogen content	Percent	0	3	minimal	minimal	0

Abbreviations: N/A, not applicable; N/P = not provided.

<sup>a</sup>Values based on the following dewatered solids characteristics: total solids—28%; combustible solids (CS)—75%; higher heating value—23,260 kJ/dry kg CS; carbon—57% of CS; hydrogen—7% of CS; oxygen—30% of CS; nitrogen—5% of CS; sulfur—1% of CS.

<sup>b</sup>Normalized to feed rate at maximum size offered by the equipment supplier.

<sup>c</sup>Heat recycled to sustain the process.

<sup>d</sup>Natural gas equivalent.

<sup>e</sup>Amount required to self-sustain process.

<sup>f</sup>Author-calculated value based on 5 MW power generation quoted by the supplier at 204 dry tonne/d at 20% total solids and assuming 40% power production efficiency, combustible solids, and heating values as noted. Value is conservative as it ignores energy radiation losses, latent heat of vaporization for water resulting from the combustion of off-gas, and heat demand to raise combustion air to process temperature.

<sup>g</sup>Supplier recycles a portion of energy as cleaned off-gas in addition to heat recovery from the flue gas. Value estimated using the heating value of cleaned off-gas, actual energy recovered percentage is higher if the latent heat of water vapor from combustion is included but was not available.

TABLE 3 Chemical properties of sludge- and biosolids-derived char

Parameter <sup>a</sup>	Unit	Biosolids/ sludge						Land Application Limits EQ/Ceiling
		300°C	400°C	500°C	600°C	700°C		
pH <sup>b,j</sup>		4.4–7.2	5.3–7.3	4.9–8.5	6.5–9.8	8.1–12	8.4–12	
Surface Area <sup>b,e,j</sup>	m <sup>2</sup> /g	2.2–18	5.3–20	0.1–23	3.2–52	12–27	27	
Carbon <sup>b,f,h,j</sup>	wt.%	21–38	23–27	20–23	18–21	20–21	20	
Nitrogen <sup>b,f,h,j</sup>	wt.%	3.0–5.4	3.3–6.1	2.4–3.8	1.8–3.1	1.5–2.7	0.91–1.2	
Phosphorus <sup>b,e,f,h,j</sup>	wt.%	1.5–5.2	3.5–4.1	3.4–4.3	3.6–6.1	4.5	4.9	
Potassium <sup>b,e,f,h,j</sup>	wt.%	0.08–0.75	0.11–0.75	0.22–0.90	0.13–1.0	0.26–1.3	1.7	
Sulfur <sup>b,z,j</sup>	wt.%	0.67–5.2	0.62–4.5	0.61–4.7	0.50–5.9	0.55–0.87	6.2	
Zinc <sup>b,j</sup>	mg/kg	306–2,580	321–1,417	986–2,572	411–2,822	1,090–3,368	1,090–2,175	2,800/7,500
Copper <sup>b,j</sup>	mg/kg	115–1,218	152–1,150	213–1,551	138–1,674	209–1,697	227–1,500	1,500/4,300
Lead <sup>b,j</sup>	mg/kg	20–3,740	115–4,410	83–4,900	93–5,120	111–5,250	132–5,200	300/840
Nickel <sup>c,e,s,j</sup>	mg/kg	23–112	50–182	95–165	35–292	101–219	103–195	420/420
Cadmium <sup>c,e,j</sup>	mg/kg	BDL – 169	2.6–197	2.8–225	3.2–235	229	3.2–123	39/85
Arsenic <sup>c,e,h,j</sup>	mg/kg	<3–26	<3–27	<3–31	<3–32	35	<3–37	41/75
Selenium <sup>c</sup>	mg/kg	<6.6	<6.6	<6.6	<6.6	<6.6	<6.6	
Chromium <sup>b,s,h,j</sup>	mg/kg	20–449	79–108	61–665	61–1,065	106–1,374	83–103	
Manganese <sup>b,d,f,j</sup>	mg/kg	56–748	58–494	536–731	80–1,076	1,383		
Cobalt <sup>b,e,j</sup>	mg/kg	2.1–20	16–22		19–25			
Reference(s)		b–i	b, c, f, i, j	c, d, f, h, i	b–d, f, j	d, f, i	c, i	USEPA (1993)

<sup>a</sup>Showing range of reported values for biosolids/sludge and different pyrolysis temperatures. BDL = below detection limit. EQ = exceptional quality.

<sup>b</sup>de Figueiredo et al. (2019).

<sup>c</sup>Hossain et al. (2011).

<sup>d</sup>Jin et al. (2016).

<sup>e</sup>Khan, Chao, et al. (2013).

<sup>f</sup>Lu et al. (2013).

<sup>g</sup>Méndez et al. (2012).

<sup>h</sup>Song et al. (2014).

<sup>i</sup>Yuan et al. (2015).

<sup>j</sup>Chagas et al. (2021).

nutrient availability (Jeffery et al., 2011; Jellali et al., 2021; Racek et al., 2020). Increasing pyrolysis temperatures increase sludge- and biosolids-derived char pH, surface area, pore-volume, total phosphorus (TP), and potassium (K) concentrations and decrease nitrogen (N) concentrations (Table 3). Therefore, targeting specific char characteristics could be achieved by using select temperatures. For example, land applying biosolids-derived char (produced at 300°C and 500°C) at 15-tonnes/ha to a moderately acidic soil increased pH, TP, and corn grain yield and did not result in an accumulation of heavy metals, indicating that char could be a suitable replacement for mineral fertilizers (de Figueiredo et al., 2019, 2020). Sludge-derived char (produced at 600°C) applied at 1.7-tonnes/ha was also beneficial to moderately alkaline soils, increasing TP and K concentrations and corn yield while decreasing the uptake of metals (Xie et al., 2021).

In char, nutrients, such as N, phosphorus (P), K, and sulfur (S), follow different fate pathways during thermal processing. Up to 40% of the N in biosolids can be lost to the gas phase, primarily as ammonia and hydrogen cyanide, at temperatures up to 800°C (Chen et al., 2011; Wei et al., 2015). Similarly, Hossain et al. (2011) found that up to 40% of S volatilized with increasing temperatures. P and K, however, become concentrated in char on a mass concentration basis as biomass is lost (Table 3; Lu et al., 2013; Yuan et al., 2015). TP concentrations in biosolids-derived char increased by 40% to 50% at 700°C, indicating P was associated with the inorganic fraction of biosolids (Hossain et al., 2011; Yuan et al., 2015).

The pyrolysis and gasification of sludge and biosolids volatilize a small portion of heavy metals in the feedstock; however, the remainder is concentrated in the char due to the loss of biomass (Chanaka Udayanga et al., 2018). Pyrolysis of sludge and biosolids results in a

reduction of leaching and bioavailability to plants relative to the feedstock (Jin et al., 2016; Lu et al., 2016). Méndez et al. (2012) demonstrated that sludge pyrolysis decreased the plant-available and mobile forms of nickel (Ni), zinc (Zn), copper (Cu), and lead (Pb). When blended with agricultural soil, the leaching of Cu, Ni, cadmium (Cd), and Zn from char was lower relative to raw sludge. This enhanced sorption is attributed to the large surface area, porous structure, and complexation with surface functional groups and has also been shown to reduce the uptake of polycyclic aromatic hydrocarbons (PAHs) by plants and remove micropollutants, including metals, hormones, and pharmaceuticals and personal care products (PPCPs) from wastewater (Khan, Wang, et al., 2013; Kimbell et al., 2018; Tan et al., 2015; Tong et al., 2019).

Char has agronomic value, mainly due to the carbon, nutrients, and liming effect when blended with soils. Char has also been shown to have carbon capture and sequestration benefits that are being investigated (Callegari & Capodaglio, 2018; Patel et al., 2020). Char may also be used directly in wastewater treatment, taking advantage of its contaminant sorption properties (Xie et al., 2021); however, Tong et al. (2016) found that the sorption capacity of biochar for triclosan in secondary effluent was suppressed due to the presence of total suspended solids and other organic constituents. Racek et al. (2020) noted that char from organic material is too valuable for land application and can be used to store volatile nutrients, as an absorber for removing odor, insulating material in the building industry, energy storage in batteries, and filters for landfills. Because of the potential value of char, several pyrolysis system suppliers indicated that they would manage char at no cost, and one indicated the potential for profit-sharing.

### Air emissions

Pyrolysis and gasification technologies include a gas-phase output that requires treatment to meet air emissions regulations. WEF (2009) provided a general overview of the permitting process for sewage sludge incinerators which would generally apply to pyrolysis and gasification systems. Pyrolysis and gasification technologies are not classified under the USEPA (2011) Sewage Sludge Incineration Rule, 40 C.F.R. § 60, but each installation requires a site-specific applicability determination ruling from the USEPA. However, recent action by the USEPA may lead to the promulgation of future regulations (USEPA, 2021b) for these technologies.

Contemporary air pollution control systems can be configured to meet regulatory emissions limits. System suppliers have a wide array of air pollution control

equipment options to meet emission criteria. Potential equipment for use with pyrolysis and gasification systems is covered in depth in combustion-based references (Niessen, 2002; WEF, 2009). The pyrolysis facility currently operating in the US and the gasification facility that recently completed its trial operation both employ similar air pollution control equipment to meet regulatory limits and prove system performance for future applications. In either case, the thermal oxidizer combusts the off-gas from the thermal reactors, converting organic pollutants to CO<sub>2</sub> and H<sub>2</sub>O at high efficiency (Niessen, 2002). Subsequently, wet scrubbers collect particulate and acid gases. The gasification facility uses a cyclone upstream of the wet scrubber to capture particulates. Before atmospheric discharge, an activated carbon filter provides the final cleaning step—mercury (Hg) and trace organic compound removal.

By operating at substoichiometric oxygen levels, pyrolysis and gasification technologies offer a unique opportunity to minimize nitrogen oxide (NO<sub>x</sub>) emissions. In contrast, other common pollutants require air pollution control processes to meet regulatory limits (Winchell et al., In Review). Thermal- and fuel-bound mechanisms produce NO<sub>x</sub> in thermal processes, with the former being insignificant at temperatures less than 1,093°C when processing WRRF sludge or biosolids (WEF, 2009). The fuel-bound mechanism requires oxygen in the presence of N in the sludge or biosolids to produce NO<sub>x</sub>. Fuel-bound N primarily converts to N<sub>2</sub> and ammonia (Basu, 2013). Pyrolysis and gasification systems may also sequester some N in the char (Tables 2 and 3), limiting NO<sub>x</sub> emissions.

## UNREGULATED CHEMICAL REMOVAL AND DESTRUCTION

The potential for pyrolysis and gasification to provide onsite destruction of PFAS and other emerging pollutants in sludge or biosolids warrants industry interest. The significant reduction or complete removal of these chemicals from sludge- or biosolids-derived char may assist WRRF land application or beneficial reuse programs. While some work has been advanced to fully elucidate these chemicals' fate and transformation products in the residuals, oils, and gases from thermal treatment technologies to enable proper management, additional research is needed.

### PFAS

Significant emphasis has been placed on PFAS in sludge and biosolids due to their ubiquitous detection

throughout the environment and recalcitrant nature (Winchell et al., 2022). Kim et al. (2015) conducted pyrolysis experiments with wastewater solids at laboratory scale at 300°C and 700°C, finding no significant change of PFAS in the biochar. By contrast, Kundu et al. (2021) demonstrated removal of all measured PFAS species in a municipal biosolid sample to non-detect levels in char at temperatures ranging from 500°C to 600°C. Xiao et al. (2020) investigated the thermal stability of several PFAS on granular activated carbon (GAC) in various reducing atmospheres. The study observed that more than 80% of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) adsorbed on GAC was converted to fluoride ions at temperatures exceeding 700°C, and concentrations of both compounds were reduced by more than 99.9%. In a recent study, at temperatures of 500°C, Williams et al. (2021) found, in unreviewed research, three of 28 targeted PFAS species, of nearly 8,000 compounds in the PFAS family (USEPA, 2020), could be detected, all at less than 0.5 parts per billion (dry weight), or µg/kg, in the resulting biochar and the 28 PFAS were removed to non-detect levels at 700°C. While this study showed promise for a handful of the PFAS that are potentially present in sludge or biosolids, further study is needed to validate PFAS removal at full-scale as it is expected that the feedstock size, char hold time at pyrolysis temperature, and char porosity may impact heat diffusion through the feedstock and overall PFAS removal rates. Thoma et al. (2021) presented the first PFAS removal results from a full-scale pyrolysis system processing dried biosolids. This research analyzed 41 PFAS in the dried biosolids and biochar. The study measured 21 PFAS ranging in concentration from 2 to 85 µg/kg in the dried biosolids. No PFAS were detected in the biochar, resulting in 81.3% to 99.9% removal when using the method detection limit concentration. The researchers identified hydrogen fluoride (HF), tetrafluoromethane (CF<sub>4</sub>), and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) in the flue-gas after the thermal oxidizer but disagreement in results of different test methods and potential contamination prevented the authors from making definitive conclusions. Indirect measurements of the gas-phase PFAS in the drain from the wet scrubber used for air emissions control erratically detected PFOA but all samples contained measurable amounts of perfluorooctane sulfonamide (PFOSA) with the latter not co-identified in the dried biosolids. The authors hypothesized the PFOSA detection may have resulted from the more sensitive analytical method applied to the scrubber water compared to the dried biosolids but needs further investigation. In addition to the transformation through pyrolysis or gasification processes, the boiling point data for PFAS suggest they are retained with the solids

through the prerequisite drying step; however, some transformation between compounds has been hypothesized by comparing the feedstock and dried product (Kim Lazcano et al., 2020).

Williams et al. (2021) analyzed the pyrolysis off-gas stream for 31 specific PFAS in a bench scale setting. They found that the limited detection resulted in a combined mass removal efficiency of 84.4% and 95.6% of measured PFAS, including that found in the char at the two experimental temperatures. Pyrolysis and gasification provide opportunities to thermally decompose PFAS, which has been demonstrated in oxygen-deficient conditions at temperatures as low as 600°C (Taylor & Yamada, 2003; Yamada et al., 2005). And, while the formation of elemental hydrogen and resulting thermal cracking reactions in a gasifier may enhance the destructive potential via hydrodefluorination, the presence of several organofluorine transformation products, including simple perfluorinated compounds, have also been identified in the off-gas (Yamada et al., 2005). Further analysis of the extent to which transformation products are present is required to assess the efficacy of pyrolysis or gasification as a standalone treatment option. Further, many of the smaller, perfluorinated by-products require higher temperatures for degradation than the parent compounds (Winchell, Ross, et al., 2021). Thus, generating substantially more mobile PFAS transformation products in the off-gas is a risk.

The direct combustion of pyrolysis and gasification off-gases provides a promising opportunity to fully oxidize PFAS transformation products with subsequent removal of the hydrogen fluoride in downstream air pollution controls. The direct combustion systems used with pyrolysis and gasification to date include thermal oxidizers such as those permitted as the best available control technology (BACT) for PFAS treatment from emissions at the Saint-Gobain Performance Plastics (SGPP) and Chemours industrial facilities (Beahm, 2019; Focus Environmental Inc., 2020). These facilities are required to maintain a minimum combustion temperature of 980°C with initial residence times proposed from 0.75 to 1.2 s. Initial stack testing at Chemours suggests these operating conditions meet the 99.99% destruction efficiency of specific PFAS as mandated by permit (Focus Environmental Inc., 2020). In addition, targeted and non-targeted PFAS analyses of pyrolyzer/gasifier off-gas and thermal oxidizer flue gas utilizing fluorine balance techniques such as total organic fluorine (TOF) can be conducted to verify destruction (Winchell, Wells, et al., 2021). Therefore, developing and validating laboratory-scale pyrolysis or gasification and a direct combustion system with commercial-scale applications could provide the industry a valuable tool to evaluate various operating parameters at a smaller scale and reduced cost.



## Other chemicals

Unregulated chemicals, including PPCPs, steroids, hormones, and other emerging pollutants, have been detected in wastewater effluent, sludge, and biosolids (McClellan & Halden, 2010; Patel et al., 2019; USEPA, 2009). Some of these chemicals can be fully or partially degraded by conventional wastewater treatment processes, but others remain in the effluent or partition to sludge and biosolids (Kinney et al., 2006; Luo et al., 2014; Spongberg & Witter, 2008; Walters et al., 2010). Sorption potential was identified as a primary factor governing chemical persistence in biosolids (Heidler & Halden, 2008). PPCPs with log  $K_{ow}$  values greater than 5.2 or log  $K_{oc}$  values greater than 4.4 were predicted to have the greatest persistence in biosolids.

PPCPs frequently detected in biosolids include triclocarban, triclosan, miconazole, tetracycline, 4-epitetracycline, norfloxacin, ciprofloxacin, doxycycline, paroxetine, and ofloxacin (Guerra et al., 2014; USEPA, 2009). McClellan and Halden (2010) determined mean concentrations of 72 PPCPs from 110 biosolids samples and identified triclocarban, triclosan, ciprofloxacin, ofloxacin, 4-epitetracycline, tetracycline, minocycline, and diphenhydramine as having the highest concentrations. In 2016, however, the U.S. Food and Drug Administration issued a final rule establishing that 19 specific ingredients, including triclosan and triclocarban, were no longer generally recognized as safe and effective, prohibiting companies from marketing soaps as antibacterial if they contain one or more of these ingredients. Brose et al. (2019) reported that companies promptly removed these compounds from products with a 70% decrease in triclosan and triclocarban in per capita influent loading into seven WRRFs from 2012 to 2017. There was a corresponding 70% decrease in triclosan and an 80% decrease in triclocarban concentrations in biosolids.

Most studies evaluating the ability of pyrolysis to remove unregulated chemicals have been conducted using temperatures below 600°C. For example, Mercl et al. (2021) tested 69 pharmaceuticals from 27 drug classes in biosolids. They found that pyrolysis at 420°C resulted in concentrations for all pharmaceuticals below detection limits in the char. Similarly, Moško et al. (2021) reported that temperatures as low as 400°C were sufficient to transform amitriptyline, caffeine, carbamazepine, diclofenac, dosulepin, hydrochlorothiazide, ibuprofen, metoprolol, and saccharin to below detection limits. Ross et al. (2016) reported that pyrolysis removed the antimicrobials triclosan and triclocarban to below the quantification limits at 300°C and 200°C, respectively. They also found that nonylphenol, an endocrine-disrupting compound, was removed at 600°C. Endocrine disruptors and hormones

were effectively removed from biosolids with pyrolysis at temperatures as low as 400°C, with removal efficiency increasing with temperature (Hoffman et al., 2016; Moško et al., 2021). Ni et al. (2020) tested pyrolysis at temperatures between 150°C and 500°C and recommended at least 450°C to remove microplastics present in biosolids. PAHs and polychlorinated biphenyls (PCBs) were removed with pyrolysis; however, temperatures over 600°C were required to achieve removal efficiencies greater than 99.8% (Moško et al., 2021). Kimbell et al. (2018) demonstrated that pyrolysis of biosolids at 500°C and higher resulted in approximately 6-log removal of antibiotic-resistant genes. These studies suggest that pyrolysis is a practical treatment pathway for transforming unregulated contaminants. As discussed previously, the emerging pollutants of interest in the sludge or biosolids will likely be retained through the upfront drying step due to evaporative cooling; the process temperature is often maintained below 80°C.

The fate of emerging pollutants during the thermal treatment of sludge and biosolids is not fully understood. Although studies have shown that thermal treatment effectively transforms many unregulated chemicals from the solid phase, there is a lack of data regarding concentrations of these chemicals and their transformation products in the resulting oils and off-gases. Studies have suggested that PPCPs, PAHs, PCBs, endocrine disruptors, and hormones either volatilize or decompose due to their physicochemical properties (Moško et al., 2021; Ross et al., 2016). Ross et al. (2016) found that compounds with higher vapor pressures were more likely to volatilize while compounds with lower vapor pressures had longer retention times and were more likely to be transformed; reductive dehalogenation was suggested as a mechanism for the transformation of triclocarban. Hu et al. (2020) investigated the concentration of 16 PAHs in pyrolysis products from different sewage sludges. They found that most PAHs were formed during pyrolysis and mainly ended up in the oil and off-gas with higher temperatures, promoting more significant PAH formation in the oil. Like the fate of PFAS through pyrolysis, the coupling of a thermal oxidizer leads to extensive destruction of the volatilized PAH compounds, but further research must be completed to verify this finding.

## CONCLUSIONS

The suppliers surveyed as a part of this work prove that the interest in pyrolysis and gasification technologies to process WRRF sludge or biosolids continues despite historical challenges. The quintessential benefit of these technologies is reducing the amount of mass requiring

subsequent management or disposal. This mass also has properties supporting beneficial reuse applications if reliable markets can be adequately developed. Potential transformation or destruction of emerging pollutants such as PFAS also increases their attractiveness to WRRF facilities looking for proactive solutions or hedging against future regulations. The processes identified can utilize the energy present in the sludge and biosolids to satisfy the thermal requirements.

While promising, these technologies are just entering the US market. Of the suppliers surveyed, three have a single system that can be considered full scale, while the others are in construction or pilot scale development. These suppliers have also noted several additional full-scale facilities in construction or development, indicating the industry will soon have several examples to evaluate. Detailed evaluation of these facilities for several years after startup is recommended to determine whether operation and maintenance requirements, reliability, performance, energy recovery, and other aspects generally warrant widespread adoption of the technology. Nevertheless, with the current pyrolysis and gasification installations and those being planned, the wastewater treatment industry has three high-temperature alternatives for sludge or biosolids processing.

#### ACKNOWLEDGMENTS

Martha J.M. Wells of EnviroChem Services provided review and editorial assistance for the development of this article.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

#### AUTHOR CONTRIBUTIONS

**Lloyd Winchell:** Conceptualization; data curation; formal analysis; investigation; methodology; project administration; supervision. **John Ross:** Conceptualization; data curation; formal analysis; investigation; methodology; visualization. **Dominic Brose:** Conceptualization; data curation; formal analysis; investigation; methodology. **Thais Pluth:** Conceptualization; data curation; formal analysis; investigation; methodology. **Katherine Bell:** Conceptualization; project administration.

#### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### ORCID

Lloyd J. Winchell  <https://orcid.org/0000-0003-1666-8681>

Dominic A. Brose  <https://orcid.org/0000-0002-7220-7866>

Thais B. Pluth  <https://orcid.org/0000-0002-5851-9476>

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**How to cite this article:** Winchell, L. J., Ross, J. J., Brose, D. A., Pluth, T. B., Fonoll, X., Norton, J. W. Jr., & Bell, K. Y. (2022). Pyrolysis and gasification at water resource recovery facilities: Status of the industry. *Water Environment Research*, 94(3), e10701. <https://doi.org/10.1002/wer.10701>





BY JOHNATHON SHEETS & MADDISON LEDOUX | SEP 10, 2021

## ADDRESSING THE IMPACTS OF PFAS IN BIOSOLIDS

An overview of regulations, treatment & challenges surrounding PFAS in biosolids



In recent years, per- and polyfluoroalkyl substances (PFAS) (<https://www.wwdmag.com/contaminants/pfas->

101-forever-chemicals-drinking-water) have become a topic of public concern, particularly when discovered in drinking water supplies. PFAS are a family of more than 3,000 man-made chemicals that have been manufactured and used since the 1940s. This large class of fluorosurfactants have unique chemical and physical properties, which make them extremely persistent, as well as mobile, in the environment.

The carbon-fluorine (C-F) bond in PFAS is the strongest bond in chemistry which does not break down naturally in the environment. Long-chain PFAS, specifically perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been phased out since 2002. Many replacement compounds are poly-fluorinated and could degrade into precursors of long-chain legacy compounds. The prevalence of PFAS in the environment has raised concerns about the possibility of their adverse health impacts. An illustrative example of a PFAS molecule is shown in Figure 1.

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## PFAS in Biosolids

PFAS compounds are not directly generated at water resource recovery facilities (WRRFs), but rather enter WRRFs from other sources. Examples include through wastewater generated at industrial facilities that produce or process PFAS, through leachate from landfills that contain PFAS-laden wastes, through municipal wastewater with background levels of PFAS and through contaminated storm water, among others. According to the Interstate Technology Regulatory Council (ITRC), typical treatment methods at WRRFs do not remove or destroy PFAS, and a portion of those compounds may partition to sludge. Figure 2 describes the PFAS fate and transport at a typical WRRF.

Common sludge treatment (<https://www.wwdmag.com/sludge-dewatering/what-activated-sludge>) processes, such as lime treatment, digestion, thermal drying, and composting do not reduce PFAS in sludge. Therefore,

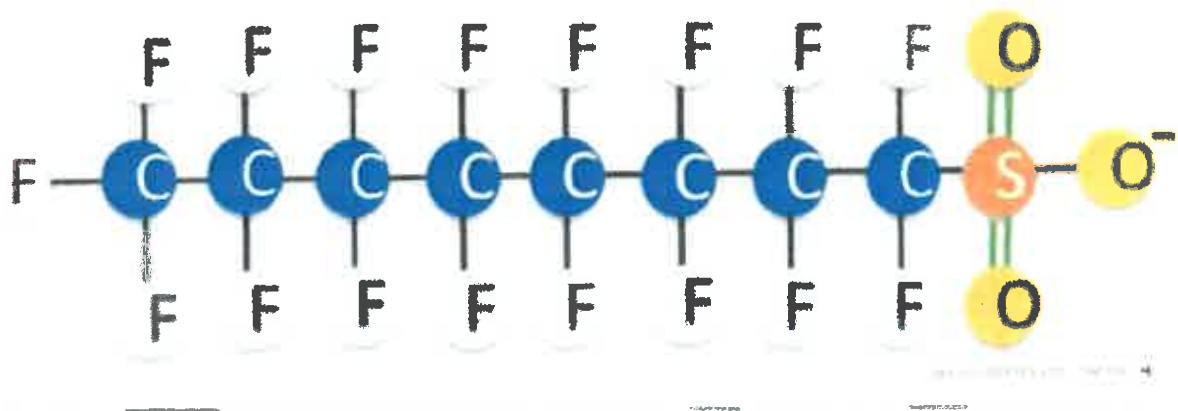
PFAS are present in both plant effluent and in biosolids at U.S. WRRFs. The most common PFAS compounds in sludge are PFOS (<10 to 1,100 ng/g dry weight) and PFOA (1 to 240 ng/g dry weight). As expected, the concentration of PFAS in biosolids is higher at WRRFs that serve industrial customers.

In 2004, a North East Biosolids and Residuals Association (NEBRA) survey showed that approximately 55% of wastewater solids are recycled to soils as biosolids, about 30% are landfilled, and about 15% are incinerated. Each of these management options may lead to environmental releases of PFAS. For example, PFAS may transport from landfilled solids to groundwater (unlined landfills) or leachate (lined landfills). Low temperature incineration may cause PFAS to be transferred from the solid matrix to the air. PFAS may also be released from land applied biosolids to the soil matrix, groundwater (<https://www.wwdmag.com/groundwater?type=All&page=1>) or surface runoff (<https://www.wwdmag.com/industrial-water-wastes-digest/asphalt-company-fails-protect-river-runoff>).

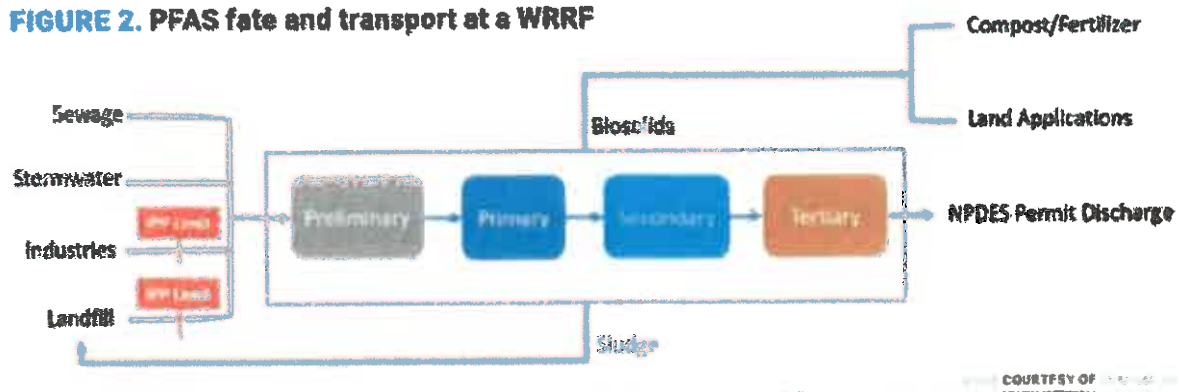
However, the fate and transport of PFAS from biosolids is dependent on several factors. The type and concentration of PFAS must be well understood since the compounds are known to have varying physical and chemical properties. Site characteristics, such as soil properties, weather patterns, plant uptake, and

biosolids application methods, impact environmental transport of PFAS. Agencies such as the U.S. EPA Office of Research and Development, the Water Research Foundation (WRF), and several others are investing in research to improve knowledge of PFAS transport and provide guidance to regulators.

**FIGURE 1. PFAS molecule**



**FIGURE 2. PFAS fate and transport at a WRRF**



# PFAS Regulations & Impacts on Biosolids

In 2016, the EPA published Drinking Water Health Advisories for PFOA and PFOS at a combined level of 70 parts per trillion (ppt). In February 2019, EPA issued its PFAS Action Plan that included a goal to move forward with a regulatory determination for PFOA and PFOS limits in drinking water. Many states adopted their own regulations, typically at levels below the 70 ppt health advisory level. Implementation of drinking water limits have impacted biosolids (<https://www.wwdmag.com/biosolids-management?type=All&page=0>) beneficial use programs at WRRFs.

At the federal level, regulations have not been promulgated for PFAS in biosolids. The state-specific regulations and guidelines involve concentration limits of different PFAS compounds in drinking water, groundwater, and, in a few cases, surface water. Only Maine has imposed a limit on three PFAS compounds in biosolids.

As of July 2021, there is no EPA approved method for sampling PFAS in biosolids. Meanwhile, drinking water limits have been imposed on biosolids due to the fear that PFAS may migrate to groundwater. Despite the lack of clear guidance, active investigation of biosolids treatment technologies for PFAS removal is underway.

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## Treatment Alternatives for PFAS in Biosolids

Several treatment and mitigation options can be considered when addressing PFAS in biosolids. While source reduction is the most cost effective and efficient solution, existing and emerging technologies are available. It is anticipated that future regulatory action will streamline research and development of technologies to reduce PFAS from biosolids. Treatment alternatives include the following.

**Source Reduction.** The strength of the C-F bond increases the ability to bioaccumulate and not readily degrade. Therefore, the easiest and most cost-effective method to reduce PFAS in biosolids is to mitigate discharges to the WRRF. This could be achieved via 1) reduction of point source discharges from industry; and 2) reduction in background concentrations via drinking water treatment. Both can be achieved through regulatory action, such as setting a PFAS limit via Industrial Pretreatment Programs (IPP), or setting drinking water limits.

**Incineration.** As of July 2021, thermal destruction is the preferred treatment technology to remove PFAS from biosolids, since high temperatures are needed to break the C-F bond. Incineration is the combustion of residual solids to ash and combustion gas and is commonly used for the destruction of persistent organics from hazardous waste. The EPA is actively investigating the time temperature regimes needed to remove PFAS via biosolids incineration. Packaged dryer-incinerators are also available for on-site biosolids destruction and waste heat recovery at WRRFs. A combined dryer-incinerator could be an energy efficient method to destroy PFAS while generating an end product (ash) that has lower mass and volume. However, incinerator systems are expensive and must meet stringent air permitting requirements. A photograph of a biosolids incinerator stack is shown in Figure 3.

Several emerging sludge treatment technologies exist that could meet the goal of reducing biosolids disposal costs and PFAS mitigation. Emerging technologies include pyrolysis, gasification, and supercritical water oxidation and are described in more detail below.

**Pyrolysis/Gasification.** Pyrolysis is the thermal decomposition of materials at high temperatures (greater than 450 to 500°C) in the absence of oxygen. The process involves treating dried sewage sludge in a closed pressurized high-temperature reactor vessel. The final products include pyrolysis gas ( $H_2+CO+CO_2+others$ ), bio-oil and biochar. The benefit of pyrolysis is that it further reduces the mass of feedstock and products can be used for energy production (gas, oil) or agricultural land application (biochar). The disadvantages of the technology are that it is relatively unproven with sludge in the U.S., that it has a higher cost than other thermal technologies, and that the operating temperatures (450 to 600°C) are lower than the combustion temperatures of most PFAS compounds (greater than 1,000°C). There are ongoing studies however, that are evaluating pyrolysis for its PFAS destruction potential.

Gasification is the thermal decomposition of materials at high temperatures in the presence of low oxygen levels. Process temperatures are typically higher than pyrolysis, and the products are limited to syngas and biochar/ash. Pyrolysis and gasification have been claimed as methods to reduce PFAS from biosolids. However, further research on fluorine mass balance is needed to understand how PFAS degradation products partition to products.

**Supercritical Water Oxidation.** Supercritical water oxidation (SCWO) refers to the process that leverages supercritical water for complete oxidation of organic compounds in sludge. In the presence of oxygen, organics can be converted to clean water, inert gases, mineral salts and reusable heat.

There are several benefits to SCWO. First, nearly 99% of the incoming solids are reduced in seconds. Second, the process can be fed with sludge at 10 to 15% solids. Third, the carbonaceous end product is carbon dioxide, the nitrogenous end product is  $N_2$  (temperature is too low for  $NO_x$ ), and the sulfurous end product is  $CaSO_4$  (temperature is too low for  $SO_x$ ), so air permitting concerns are minimal. Finally, the system has been shown to break the C-F bond in PFAS.

The drawback of the system is that there are no known commercial installations at WRRFs. Additionally, there are likely high energy demands to start the system (though the reaction is self-sustaining after startup).



# Biosolids Cost Impacts of PFAS

A collaborative team, including CDM Smith, NEBBRA, WEF and NACWA, completed the Cost Analysis of the Impacts on Municipal Utilities and Biosolids Management to Address PFAS Contamination. The research team surveyed WRRFs, biosolids management companies, and end use facilities (incineration, composting, landfills, farms) to estimate the cost and operational impacts from pending or active PFAS regulations.

When the study was published in 2020, the results showed that in areas where PFAS regulations have been implemented, biosolids management costs have increased by an average of 37%. As more data from those same surveyed facilities has been collected in 2021, the management costs at WRRFs with PFAS regulations have increased to an average of 72%. Some of the states which have seen the greatest impact include Arizona, Michigan, Maine and New Hampshire.

The rapid cost increases have been attributed to reduced land application availability due to PFAS and to the use alternative high-cost disposal sites such as landfills.

Meanwhile, cost impacts have been minimal at WRRFs that manage their own biosolids, do not rely on beneficial reuse, and/or at WRRFs located in areas without PFAS regulation. These results clearly show that local, state, or federal PFAS regulations have a significant impact on the costs of biosolids management.

## Summary

Many WRRFs in the U.S. are proactively evaluating solutions to mitigate PFAS. Source reduction is the most cost effective and efficient solution, and several WRRFs in New England are working are considering PFAS limits on industry. Additionally, it is anticipated that drinking water limits will reduce the background concentration of PFAS that enters WRRFs.

In areas with already limited land application or landfill capacity, such as New England, WRRFs are currently evaluating incineration as a viable disposal option. However, in these areas, incineration capacity is lacking, which drives up costs. As a result, WRRFs are evaluating methods to reduce the total mass of biosolids that must be managed, such as sludge drying. Implementation of sludge drying offers the potential to produce a low volume, Class A biosolids product that could be cost-effectively transported to states with less strict land application requirements. Several WRRFs in the Midwest are also considering sludge drying to regain control and flexibility in their biosolids management programs.

To date, there are few known installations of emerging technologies such as pyrolysis, gasification and SCWO. It is anticipated that future regulatory action will streamline research and development of

technologies to reduce PFAS from biosolids.

## POTENTIAL PFAS DESTRUCTION TECHNOLOGY: PYROLYSIS AND GASIFICATION

In Spring 2020, the EPA established the PFAS Innovative Treatment Team (PITT). The PITT was a multi-disciplinary research team that worked full-time for 6-months on applying their scientific efforts and expertise to a single problem: disposal and/or destruction of PFAS-contaminated media and waste. While the PITT formally concluded in Fall 2020, the research efforts initiated under the PITT continue.

As part of the PITT's efforts, EPA researchers considered whether existing destruction technologies could be applied to PFAS-contaminated media and waste. This series of Research Briefs provides an overview of four technologies that were identified by the PITT as promising technologies for destroying PFAS and the research underway by the EPA's Office of Research and Development to further explore these technologies. Because research is still needed to evaluate these technologies for PFAS destruction, this Research Brief should not be considered an endorsement or recommendation to use this technology to destroy PFAS.

### Background

Various industries have produced and used per- and polyfluoroalkyl substances (PFAS) since the mid-20th century. PFAS are found in consumer and industrial products, including non-stick coatings, waterproofing materials, and manufacturing additives. PFAS are stable and resistant to natural destruction in the environment, leading to their pervasive presence in groundwater, surface waters, drinking water and other environmental media (e.g., soil) in some localities. Certain PFAS are also bioaccumulative, and the blood of most U.S. citizens contains detectable levels of several PFAS (CDC, 2009). The toxicity of PFAS is a subject of current study and enough is known to motivate efforts to limit environmental release and human exposure (EPA, 2020).

To protect human health and the environment, EPA researchers are identifying technologies that can destroy PFAS in liquid and solid waste streams, including concentrated and spent (used) fire-fighting foam, biosolids, soils, and landfill leachate. These technologies should be



Figure 1. Biosolids beneficial use.

readily available, cost effective, and produce little to no hazardous residuals or byproducts. Pyrolysis and gasification have been identified as promising technologies that may be able to meet these requirements with further development, testing, and demonstrations.

### Pyrolysis/Gasification: Technology Overview

Pyrolysis is a process that decomposes materials at moderately elevated temperatures in an oxygen-free environment. Gasification is similar to pyrolysis but uses small quantities of oxygen, taking advantage of the partial combustion process to provide the heat to operate the process. The oxygen-free environment in pyrolysis and the low oxygen environment of gasification distinguish these techniques from incineration. Pyrolysis, and certain forms of gasification, can transform input materials, like biosolids, into a biochar while generating a hydrogen-rich synthetic gas (syngas).

Both biochar and syngas can be valuable products. Biochar has many potential applications and is currently used as a soil amendment that increases the soil's capacity to hold water and nutrients, requiring less irrigation and fertilizer on crops. Syngas can be used on-site as a supplemental fuel for biosolids drying operations, significantly lowering energy needs. As an additional advantage, pyrolysis and gasification require much lower air flows than incineration, which reduces

the size and capital expense of air pollution control equipment.

### Potential for PFAS Destruction

PFAS have been found in effluent and solid residual (sewage sludge) streams in wastewater treatment plants (WWTPs) (Sinclair and Kannan, 2006; Schultz et al., 2006; Yu et al., 2009; EGLE, 2020; Maine PFAS Task Force, 2020), prompting increasing concern over management of these materials. In the United States, WWTP solids have typically been managed in one of three ways: (1) treatment to biosolids followed by land-application; (2) disposal at a lined landfill; or (3) destruction (burning) in a sewage sludge incinerator. WWTP solids are rich in nutrients and the most common U.S. practice is to aerobically or anaerobically digest it to produce a stabilized biosolid product that can be land-applied as fertilizer (EPA, 1994; EPA, 2019). This is done because the nutrients in biosolids deliver nitrogen, phosphorous, and other trace metals that are beneficial for crops and soil (Figure 1).

Some states are beginning to test biosolids for PFAS contamination and to prevent land application if concentrations exceed state-specific screening levels. An increase in rejected biosolids may lead to an increased use of incineration or landfilling of wastewater solid residuals, with increased cost burdens to communities. Currently, approximately 16% of wastewater solids are incinerated (EPA, 2019). This increased amount of incineration could introduce additional costs and other environmental considerations.

New options for the treatment of PFAS-impacted WWTP solids may be found in non-incineration thermal processes, such as pyrolysis and gasification. These approaches may show promise to reduce PFAS loadings from biosolids, in some cases without destroying the beneficial use potential of the material. Gasification may also become an attractive alternative to sewage sludge incineration for reduction of WWTP solids to inert ash, with potential uses as input material in cement production and fine aggregate applications (Lynn et al., 2015).

The high temperatures and residence times achieved by pyrolysis or gasification followed directly by combustion of the hydrogen-rich syngas stream in a thermal oxidizer (or afterburner) could potentially destroy PFAS by breaking apart the chemicals into inert or less recalcitrant constituents. However, this mechanism, as well as evaluation of potential products of incomplete destruction, remain a subject for further investigation and research. It is possible that this combination of processes may be more effective at PFAS destruction than some lower temperature sewage sludge incineration processes.

The end products of both gasification and pyrolysis result in material volume reductions of over 90% compared to

the input solids, making transport and use or disposal more energy efficient and lessening the environmental impacts (e.g., lower landfill leachate PFAS loadings compared to biosolids disposal).

### Limitations and Research Gaps

Pyrolysis and gasification of biosolids are emerging treatment technologies. In the United States, one biosolids pyrolysis company is permitted for operation with three similar biosolids systems units operating in Europe (PYREG, 2019). Several biosolid gasification projects are in development in the United States, but long-term operation on this feedstock has yet to be commercially demonstrated.

Pyrolysis and gasification represent a significant financial investment compared with direct biosolid land application alternatives, and there are a number of challenges and data gaps with these technologies. However, if these issues can be overcome, these systems could provide effective means of treating PFAS in WWTP solid residuals and PFAS-impacted biosolids.

### Next Steps

The pervasiveness and resistance to degradation of PFAS have become a motivating factor to identify methods to safely manage these substances to prevent bioaccumulation within humans or the environment. Identification and validation of safe and effective approaches to reduce PFAS levels in biosolids is an important research area for EPA.

In August 2020, EPA researchers conducted a field test at a WWTP employing pyrolysis. The purpose of this limited-scope field test was to improve understanding of target PFAS levels in the pyrolysis-produced biochar compared to the input material. EPA researchers are currently analyzing samples collected during the field test and expect to publish the results in a peer-reviewed scientific journal in 2021.

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## Contacts

- Carolyn Acheson - [acheson.carolyn@epa.gov](mailto:acheson.carolyn@epa.gov)
- Marc Mills - [mills.marc@epa.gov](mailto:mills.marc@epa.gov)
- Max Krause - [krause.max@epa.gov](mailto:krause.max@epa.gov)
- Eben Thoma - [thoma.eben@epa.gov](mailto:thoma.eben@epa.gov)

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Cite this: *Environ. Sci.: Water Res. Technol.*, 2021, 7, 638

## Removal of PFASs from biosolids using a semi-pilot scale pyrolysis reactor and the application of biosolids derived biochar for the removal of PFASs from contaminated water†

Sazal Kundu,<sup>a</sup> Savankumar Patel,<sup>a</sup> Pobitra Halder,<sup>a</sup> Tejas Patel,<sup>a</sup> Mojtaba Hedayati Marzbali,<sup>a</sup> Biplob Kumar Pramanik,<sup>b</sup> Jorge Paz-Ferreiro,<sup>a</sup> Cícero Célio de Figueiredo,<sup>c</sup> David Bergmann,<sup>d</sup> Aravind Surapaneni,<sup>de</sup> Mallavarapu Megharaj<sup>f,g</sup> and Kalpit Shah<sup>\*ae</sup>

This study focuses on the conversion of biosolids to biochar and its further use in adsorbing per- and polyfluoroalkyl substances (PFASs) from contaminated water. In particular, this study aims to (a) investigate the performance of a semi-pilot fluidised bed pyrolysis unit in converting biosolids into biochar, (b) examine the ability of the pyrolysis-combustion integrated process to destruct PFASs present in biosolids and (c) study the application of biosolids derived biochar for removing PFASs from contaminated water. The semi-pilot fluidised bed pyrolysis unit demonstrated stable temperature and oxygen profiles in the reactor. The yield of biochar was found to be 36–45% at studied temperatures (500–600 °C). The produced biosolids derived biochar samples, due to their lower H/C and O/C ratio, were found to be extremely stable with an expected long (millennia) residence time in soil. It was concluded that >90% removal of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) from biosolids derived biochar could be achieved in the pyrolysis-combustion integrated process. The biosolids derived biochar demonstrated >80% adsorption of long-chain PFASs and 19–27% adsorption of short-chain PFASs from PFAS contaminated water.

Received 16th August 2020,  
Accepted 16th December 2020

DOI: 10.1039/d0ew00763c

rsc.li/es-water

### Water impact

The effectiveness of a fluidised bed pyrolysis for reducing biosolids volume and producing biochar material was demonstrated. Over 90% of PFOS and PFOA was safely removed from the resultant biochar during pyrolysis. The produced biochar was able to adsorb PFASs from contaminated water in the range of 20 to over 95%, depending on the individual PFAS considered.

## 1. Introduction

Stabilised sewage sludge, produced by wastewater treatment plants (WWTPs), is known as biosolids. This material is an unavoidable by-product that originates from households and many industries.<sup>1</sup> The rapid increase in population as well as urbanisation contributes to a continued increase in the production of biosolids.<sup>2,3</sup> Biosolids contain many macronutrients such as nitrogen, phosphorus, sulphur, potassium, calcium and magnesium as well as micronutrients such as zinc, copper, boron, molybdenum, manganese and iron.<sup>4</sup> Therefore, biosolids are attractive for agricultural applications, and the majority of this material is currently utilised for this purpose in many countries including Australia.<sup>5,6</sup> However, biosolids may contain harmful pathogens and current regulations (particularly in

<sup>a</sup> Chemical & Environmental Engineering, School of Engineering, RMIT University, Melbourne, Victoria 3000, Australia. E-mail: kalpit.shah@rmit.edu.au;

Fax: +61 3 9925 7110; Tel: +613 9925 1109

<sup>b</sup> Civil and Infrastructure Engineering, School of Engineering, RMIT University, Melbourne, Victoria 3000, Australia

<sup>c</sup> Faculty of Agronomy and Veterinary Medicine, University of Brasília, 70910-970 Brasília, DF, Brazil

<sup>d</sup> South East Water, Frankston, Victoria 3199, Australia

<sup>e</sup> ARC Training Centre for Transformation of Australia's Biosolids Resource, RMIT University, Bundoora, Victoria 3083, Australia

<sup>f</sup> Global Centre for Environmental Remediation, Faculty of Science, University of Newcastle, Callaghan, NSW 2308, Australia

<sup>g</sup> Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE), Callaghan, NSW 2308, Australia

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ew00763c

Victoria, Australia) require biosolids to be stockpiled onsite for 1–3 years to reduce pathogen levels to the highest possible treatment grade for soil amendment. Also, heavy metals, micro-plastics, pesticides, chemicals, herbicides and pharmaceutical ingredients are present in biosolids.<sup>2,3,7</sup> Recently, biosolids have been recognised as a potential source of PFAS contamination in soil and groundwater which may restrict their land application in the near future.<sup>8,9</sup>

PFASs are anthropogenic compounds and, historically, have been used in a wide range of applications including fire-fighting foams, non-stick cookware, stain- and water-repellent fabrics, polishes, waxes, paints and cleaning products.<sup>10,11</sup> To date, more than 3000 PFASs and their potential precursors have been identified<sup>12</sup> and their numbers increase with time as research progresses. Consequently, PFASs have become ubiquitous in terrestrial and aquatic environments. These chemicals are persistent, accumulative and leachable. PFOA and PFOS are the most-studied PFASs. Humans may introduce PFASs in their bodies *via* drinking contaminated water, and eating fish and meat as well as vegetables and fruits. The adverse effects of PFAS in human bodies may include, but are not limited to, increased cholesterol,<sup>13</sup> hepatotoxicity and alterations in the immune system<sup>14</sup> as well as thyroid hormone disruption.<sup>15</sup> Besides, these chemicals may cause low infant birth weights,<sup>16</sup> and they are also suspected of causing cancer.<sup>17</sup>

PFASs have been detected in WWTP influent, effluent and biosolids globally.<sup>18</sup> Hydrophobic partitioning in WWTPs is expected to result in the retention of long-chain PFASs in the sludge/biosolids.<sup>19</sup> The major PFASs in biosolids, reported in a study on US biosolids, were PFOS ( $403 \pm 127 \text{ ng g}^{-1}$  dry weight) and PFOA ( $34 \pm 22 \text{ ng g}^{-1}$  dry weight).<sup>19</sup> The other PFAS values were lower and in the range of 2 and  $26 \text{ ng g}^{-1}$  dry weight. Similar results were obtained in Australian studies.<sup>9,20</sup> PFAS management guidelines have become available in several Australian states, for example, in Victoria (regulated by EPA Victoria).<sup>8</sup> These may potentially impact the wider land application of biosolids in the near future. Therefore, a reliable and cost-effective technological platform is warranted that minimises/eliminates the PFAS risks of biosolids for land application.

PFASs have strong chemical structures, are thermally very stable and require high reaction energy/high temperatures to break down their chemical bonds. The available literature suggests that immobilisation could be the most cost-effective method for remediation of PFASs in biosolids and biosolids amended soils.<sup>21</sup> However, keeping PFASs immobilised in a solid matrix for a long time still needs to be verified by further investigation. Thermal treatments such as pyrolysis, gasification, combustion and incineration may have the potential to fully/partially destruct PFASs due to their high temperature operation conditions. Most of the studies in the literature have focused on investigating PFAS destruction through incineration.<sup>22–26</sup> Studies on the potential of pyrolysis and gasification technologies to destruct PFASs are very limited.

The pyrolysis process decomposes carbonaceous materials, such as biosolids, in the absence of oxygen.<sup>2</sup> Usually, a sweeping gas flow is provided in the pyrolysis process (except vacuum pyrolysis). In the case of fluidised bed pyrolysis, the flow-rate of the sweeping gas is high and it may be economically feasible to recycle the CO<sub>2</sub> containing hot pyrolysis/flue gas as the sweeping gas rather than using a high purity and expensive inert sweeping gas such as N<sub>2</sub>. Biochar (solid), bio-oil (liquid) and bio-gas are the three products that are generated from the pyrolysis of biosolids. The yield distribution of these products depends on a number of parameters including the composition of biosolids, pyrolysis temperature, heating/energy transfer rate, and flow rate of the sweeping gas as well as the catalyst/additive if used. Bio-oil and bio-gas could be used as fuel<sup>24,27</sup> while biochar could be used as a soil amendment material,<sup>24,27</sup> as a catalyst in the production of carbon nanomaterials<sup>28</sup> or as an adsorbent for removing micropollutants.<sup>29,30</sup> If there is a priority between biochar and bio-oil, the heating/energy transfer rate is usually considered to be tweaked. When bio-oil is considered to be the primary product, a high heating rate is applied while a slow heating rate is applied when biochar is considered to be the primary product. Previous studies suggested that pyrolysis can successfully destroy impurities such as pathogens, micro-plastics, pesticides and pharmaceutical ingredients and the products from this process can be free from these nuisances.<sup>31–34</sup> If the destruction of PFASs from biosolids can be safely performed by a pyrolysis process, it can assist water industries in reducing biosolids volume and creating an indisputable application of biosolids derived biochar as a soil amendment material as well as its other applications in chemical processing.

Pyrolysis can be carried out in both fixed bed and fluidised bed reactors. The poor gas–solid contact in fixed bed reactors may compromise the quality of biochar. Biochar with uniform characteristics is beneficial and desired, particularly if the considered end use is being a catalyst or an adsorbent. Fluidised bed reactors ensure uniform heating even at high heating rates leading to the production of high quality biochar with uniform characteristics. This opens up the possibility of extending the application of biosolids derived biochar, produced from fluidised bed reactors, in the adsorption of PFASs from contaminated water.

Several reactor designs have been evaluated in a large scale for the pyrolysis of biosolids. For instance, a microwave heating system was applied aiming to produce bio-oil as a primary product from the transformation of sewage sludge using several additives such as KOH, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>BO<sub>3</sub>, ZnCl<sub>2</sub> and FeSO<sub>4</sub>.<sup>35</sup> The technological feasibility was found to be dependent on the optimisation of process parameters and selection of appropriate additives. In a different study, sewage sludge was blended with other feedstock such as manure and studied in a fixed bed pilot-scale reactor with positive findings.<sup>36</sup> A few other pilot-scale studies were carried out using a fixed bed reactor in non-catalytic, autocatalytic or catalytic mode. However, the application of

fluidised bed pyrolysis reactors is found to be rare for pyrolysis of biosolids. In addition, pyrolysis is an endothermic process and the optimisation of energy is vital for the commercial viability of any technology. Therefore, a fluidised bed pilot scale reactor integrated with a combustion chamber, which aims to run pyrolysis in autothermal mode (*i.e.* no need for external energy), is in demand in the search for sustainable uses of biosolids.

Typically, pyrolysis of carbonaceous materials is carried out between 300 to 1000 °C.<sup>37</sup> Lower pyrolysis temperature generates biochar with a lower surface area and high oxygen containing functional groups. As the pyrolysis temperature increases, the surface area of biochar increases at the expense of functional groups. Therefore, low temperature pyrolysis is generally preferred for producing biochar for soil application while high temperature is desired when biochar with a high surface area needs to be produced. Choosing a pyrolysis temperature is challenging and a few aspects could be taken into consideration. (a) This work aims to produce biochar to be used as an adsorbent; therefore, a high surface area and an improved morphology is critical. Our previous work suggests that the pyrolysis temperature has a tremendous impact on the morphology of biochar and a pyrolysis temperature between 500 and 700 °C can generate biochar with a high porosity and surface area from biosolids.<sup>28</sup> (b) The second aspect may be the destruction of pollutants, particularly PFASs which are inherently present in biosolids. The devolatilisation and destruction of PFASs at high temperature during combustion have been established.<sup>38,39</sup> However, biosolids contain a reasonable concentration of metals and minerals that are expected to function as catalysts for the destruction of PFASs at relatively low temperature in an integrated pyrolysis-combustion process which has not been studied in the literature. (c) The third aspect may be the formation of polycyclic hydrocarbons (PAHs). Below 500 °C pyrolysis temperature, PAHs are formed *via* carbonisation and aromatisation.<sup>40,41</sup> Above 500 °C, a free radical pathway, followed by pyrosynthesis, dominates the formation of PAHs.<sup>40–42</sup> When investigating PAH formation in the pyrolysis temperature range of 100–700 °C, researchers found that the formation of PAHs is the highest in the temperature range of 400–500 °C.<sup>43,44</sup> Applying a pyrolysis temperature  $\geq 500$  °C is often suggested to minimise extractable PAHs in biochar.<sup>43,45</sup> Accounting for all these aspects, a moderate temperature range of 500–600 °C could be considered which is a trade-off between minimising PAHs and obtaining high quality biochar while assisting in the investigation of destruction of PFASs in biosolids at relatively low temperature.

PFAS contamination in ground water and industrial wastewater is a serious problem and their concentrations often reach above those set by the regulatory guidelines.<sup>46</sup> So far, granular activated carbon (GAC) from various sources (*e.g.*, coconut shell and coal) has been extensively studied for the adsorption of PFASs.<sup>46–50</sup> Biomass derived biochar has also been used in PFAS adsorption studies.<sup>51,52</sup> However, biosolids derived biochar has been rarely used in adsorption studies of PFASs.

The aim of the current study is to (a) investigate the performance of a semi-pilot fluidised bed pyrolysis unit in converting biosolids into biochar, (b) examine the ability of the pyrolysis-combustion integrated process to destruct PFASs present in biosolids and (c) study the application of biosolids derived biochar for removing PFASs from contaminated water.

## 2. Methodology

### 2.1. Pyrolysis of biosolids

**2.1.1. Biosolids sample.** The biosolids sample employed in this study was sourced from the Mount Martha Water Recycling Plant (38°16'06"S and 145°03'31"E) of South East Water Corporation, Victoria, Australia. This plant predominantly receives domestic and trade sewage, and treats sewage sludge through an activated sludge process followed by anaerobic digestion. After digestion, the solids are processed through a dewatering plant (*i.e.*, centrifuge) and solar drying facility before they are sent to stockpiling. Thus, the samples used in this study were processed through a solar dryer shed.

The biosolids sample was initially ground using a pin mill (Chenwei Machinery CW-20B) and then segregated using a vibrating screen (Sanfeng Machinery, SF-600) at FA Maker Pty. Ltd., Victoria, Australia. The pin mill and vibrating screen employed in this study are shown in Fig. S1† The biosolids, used in the trials, were 0.5–2 mm in particle size. The detailed proximate and ultimate analyses of biosolids are presented in Table 1.

**2.1.2. Description of the semi-pilot unit employed for the pyrolysis of biosolids.** The process block diagram is shown in Fig. 1 (actual image of the semi-pilot pyrolysis plant can be found in ESI† Fig. S2). Each pyrolysis trial was conducted for 5 hours. Trials were performed in triplicate ( $n = 3$  for each trial) to ensure consistency of the data and the average values are presented in this manuscript. The run mode of this system is considered as semi-continuous since the biosolids

Table 1 Proximate and ultimate analyses of biosolids

Proximate and ultimate analyses of biosolids				Ultimate analysis <sup>a</sup> (%)				
Proximate analysis <sup>a</sup> (%)				C	H	N	S	O <sup>b</sup>
Moisture	Volatiles	Ash	Fixed carbon					
11.0	60.6	29.0	10.4	38.3	4.7	6.02	0.96	21.02

<sup>a</sup> Values on a dry weight basis. <sup>b</sup> Value determined by difference.

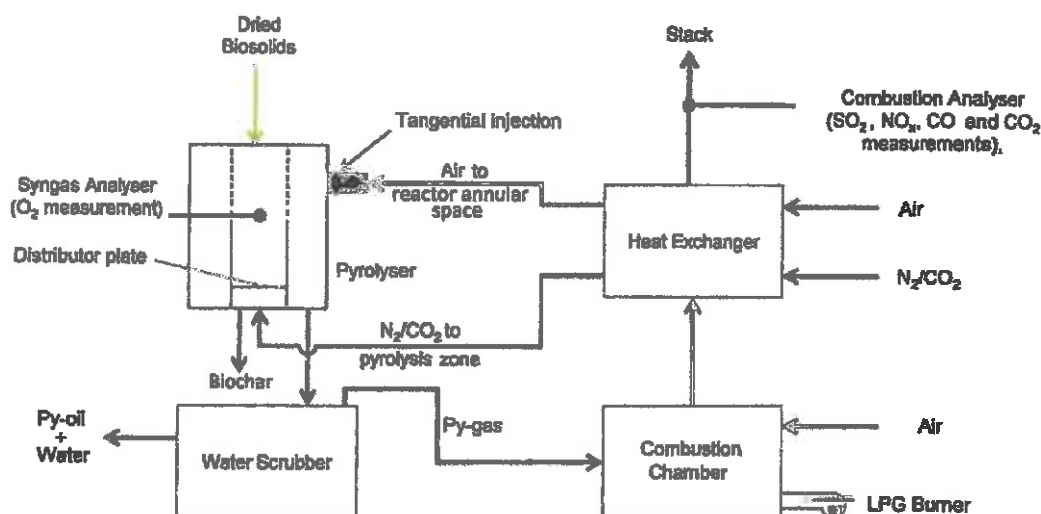


Fig. 1 Process block diagram for the semi-pilot plant setup.

were fed continuously throughout the trial period while char was collected only after the 5-hour period at the end of each trial.

During start-up, the semi-pilot plant was heated *via* a liquefied petroleum gas (LPG) burner. The hot flue gas leaving the LPG burner was used to pre-heat the gases (*i.e.* air and N<sub>2</sub>/CO<sub>2</sub>) entering the semi-pilot plant *via* a heat exchanger. The pre-heated air and N<sub>2</sub>/CO<sub>2</sub> gases were then circulated in the reactor to heat the reactor to a desired temperature. The hopper was filled with the biosolids sample at the beginning of each trial (Fig. S2†). The hopper was charged with N<sub>2</sub> *via* a N<sub>2</sub> purging line. Once the desired temperature of the reactor was attained, biosolids were continuously charged at 0.25 kg h<sup>-1</sup> from the hopper to the reactor *via* a pre-calibrated screw-feeder with continuous N<sub>2</sub> purging. The screw-feeder was calibrated for each trial.

The reactor, employed in this study, was constructed from stainless steel 253MA and insulated with ceramic fibre insulation to minimise heat losses. It was of concentric geometry, where the inner tube functioned as the pyrolyser. The bottom half of the inner tube was made of pipe, while the top half of the inner tube consisted of a wedge-wire screen. Biosolids were pyrolysed under bubbling fluidised conditions using a pre-heated N<sub>2</sub>/CO<sub>2</sub> mixed stream containing 85% N<sub>2</sub> and 15% CO<sub>2</sub>, v/v. The reason for using a N<sub>2</sub>/CO<sub>2</sub> mixed stream (85% N<sub>2</sub>, 15% CO<sub>2</sub>, v/v) in the pyrolyser was to mimic the scenario of pyrolysis in the presence of recycled flue gas. The produced gas and oil vapours from the inner pyrolyser tube were then transferred to the annular space *via* the wedge-wire screen from the top half of the reactor while the biochar produced remained at the bottom of the inner pyrolyser tube. At the end of each trial, biochar was kept further in that inner tube with an inert environment for cooling and then collected further for analysis. The annular space acted as a partial combustor for py-gas and py-oil vapours. The temperature in the annular space was

controlled by adjusting the air inlet rate. The temperature at the annular space was purposefully kept lower or equal to the pyrolysis temperature to find out whether or not PFASs are destroyed at lower temperatures in thermal systems.

By employing pre-heated air tangentially at a >10 m s<sup>-1</sup> velocity in the annular space, the py-gas and py-oil vapours were partially combusted and PFASs, if they survived in the pyrolyser, were destructed in this annular space. The remaining py-gas and py-oil vapours were rapidly transported from the annular space to a water scrubber, where they were immediately quenched. The reason for using tangential entry and high-velocity air was to ensure that the pyrolysis reaction environment is not affected and the py-gas and py-oil vapours are immediately quenched without any secondary reactions. The py-oil was condensed in the scrubber water, while non-condensable py-gas was sent to the combustion chamber of the LPG burner to ensure that it was combusted before releasing to the environment. The energy required for pyrolysis was provided by the hot air and N<sub>2</sub>/CO<sub>2</sub> gases, which were pre-heated using the combustion of LPG and py-gas (once produced). At the end of each trial, the sample from the water scrubber was collected for oil and PFAS analysis. Any PFAS species carried by the gas stream, if they survive in the pyrolysis-combustion system, should be trapped in the water scrubber. The reason is that the boiling points of PFASs, even for short chain PFASs (*e.g.*, the boiling point of pentafluorobenzoic acid (PFBA) is 220 °C), are higher than the water boiling point.

An online gas monitor (combustion analyser, MRU Optima 7) was employed to measure the concentrations of various gaseous species (CO, CO<sub>2</sub>, NO<sub>x</sub> and SO<sub>2</sub>) in the stack. The reactor was equipped with four thermocouples and they measured the following temperatures: 1) pyrolyser temperature, 2) annular space temperature, 3) reactor inlet N<sub>2</sub>/CO<sub>2</sub> stream temperature and 4) reactor inlet N<sub>2</sub> temperature. The pyrolysis trials were carried out at three different temperatures: 500, 550

and 600 °C. The average temperature at the pyrolyser thermocouple was considered as the pyrolysis temperature. The concentration of O<sub>2</sub> in the pyrolyser was continuously monitored by an online gas monitor (syngas analyser, Madur Aqua GA40T Plus). Biochar produced from biosolids in the semi-pilot trials at 500, 550 and 600 °C are labelled as BSBC-500, BSBC-550 and BSBC-600, respectively.

Biochar produced during the trial was characterised by surface imaging using a scanning electron microscope (SEM) of the Philips XL30 model and a Brunauer–Emmett–Teller (BET) analyser (Micromeritics 2000/2400). The particle size distributions of both biosolids and biochar were determined using a Malvern particle size analyser (Mastersizer 3000). Analyses related to PFAS, py-oil and heavy metals were performed externally (by ALS Limited, Australia). ALS laboratories are NATA (National Association of Testing Authorities, Australia) accredited laboratories. They have applied their WP045B, WP075A and WP0125A methods for py-oil analysis, EP231 method for PFAS analysis and WG020B for heavy metal analysis.

## 2.2. PFAS adsorption

**2.2.1. Biochar preparation for PFAS adsorption.** Biomass biochar was produced at 600 °C pyrolysis temperature to make a comparison with biosolids biochar produced at the same temperature (BSBC-600) mainly for exploring its potential to adsorb PFASs from PFAS contaminated water. The biomass biochar produced at 600 °C in this study is referred to as BMBC-600. Sawdust (predominantly Australian pine wood, sourced from a mechanical workshop at RMIT University) of the same initial particle size as the biosolids (i.e., 0.5–2 mm) was used in the production of biomass biochar. Instead of a semi-pilot plant, a muffle furnace (Barnstead Thermolyne 30400) was employed for the production of biomass biochar, where the furnace was operated at 600 °C for 1 hour. The furnace was then kept closed until it was cooled down naturally to room temperature. Afterwards, the biochar sample was taken out and stored in a desiccator. Both BMBC-600 and BSBC-600 were sieved to obtain a particle size of 0.3–0.5 mm and further employed in the PFAS adsorption study. The BET surface areas of these samples were measured and found to

be 79.87 m<sup>2</sup> g<sup>-1</sup> and 55.29 m<sup>2</sup> g<sup>-1</sup> for BMBC-600 and BSBC-600, respectively.

**2.2.2. Procedure for PFAS adsorption.** Two PFAS contaminated water samples (sources can't be revealed) were used in this study. The PFAS content in sample 1 was significantly higher than that in sample 2 (Table 2). In addition, several PFAS species in sample 2 were below the detection limit of the analytical instrument, and therefore, they were excluded from the adsorption study. The pH values of sample 1 and sample 2 were 4.3 and 7.85, respectively. In this study, we have not adjusted the pH level for the adsorption tests.

Initially, PFAS contaminated water samples were filtered through 6-micron polyethersulfone (PES) membrane filter paper to remove any suspended solids. Two adsorbents were employed to remove PFASs from these samples as detailed earlier: 1) biosolids biochar (BSBC-600) and 2) biomass biochar (BMBC-600). For each study, one gram of adsorbent was taken in a conical flask, and 50 mL of PFAS contaminated water was introduced into the conical flask. For each set of adsorption study, there was a repeat test. The tops of the conical flasks were wrapped with aluminium foil, and they were placed in an orbital shaker (Thermoline TS-400) set at 180 rpm. The samples were shaken for 48 hours. After the completion of trials, solid adsorbents were separated using 0.45-micron polyethersulfone (PES) membrane filter paper. The filtrates as well as raw samples were then sent to ALS Limited, Australia for analysis. The adsorption of PFASs by various adsorbent materials was determined using the ALS generated data.

## 3. Results and discussion

### 3.1. Process stability

Process stability with respect to important process parameters such as temperature and O<sub>2</sub> concentration is vital in obtaining products of desired quality as well as maintaining the energy balance of the semi-pilot pyrolysis unit. The integration and operation of pyrolysis–combustion has been demonstrated in fixed bed and Auger type reactor designs in the literature.<sup>53</sup> However, an integrated fluidised bed pyrolysis–combustion process has not been demonstrated yet in the literature. The present work demonstrated a stable

Table 2 Concentrations of various PFASs in contaminated water

Species	Chemical formula	Concentration (µg L <sup>-1</sup> )	
		Sample 1	Sample 2
Perfluorooctanesulfonic acid (PFOS)	F(CF <sub>2</sub> ) <sub>8</sub> SO <sub>3</sub> H	480	0.08
Perfluorooctanoic acid (PFOA)	F(CF <sub>2</sub> ) <sub>7</sub> COOH	24	0.36
Perfluorohexanesulfonic acid (PFHxS)	F(CF <sub>2</sub> ) <sub>6</sub> SO <sub>3</sub> H	210	0.61
Perfluorobutanesulfonic acid (PFBS)	F(CF <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> H	80	0.05
Perfluoropentanesulfonic acid (PFPeS)	F(CF <sub>2</sub> ) <sub>5</sub> SO <sub>3</sub> H	56	—
Perfluoroheptanesulfonic acid (PFHpS)	F(CF <sub>2</sub> ) <sub>7</sub> SO <sub>3</sub> H	20	—
Perfluorododecanoic acid (PFDoA)	F(CF <sub>2</sub> ) <sub>11</sub> COOH	0.22	—
Perfluorotridecanoic acid (PFTTrDA)	F(CF <sub>2</sub> ) <sub>12</sub> COOH	0.07	—
Perfluorotetradecanoic acid (PFTTeDA)	F(CF <sub>2</sub> ) <sub>13</sub> COOH	0.07	—



integrated fluidised bed pyrolysis–combustion system that can achieve highly stable temperature and oxygen concentration profiles. The advantage of such an integrated process is the compact design which can help reduce the capital and operating costs as well as improve the product quality.

Fig. 2 shows an illustrative presentation of the temperature profiles of various thermocouples as well as the O<sub>2</sub> concentration profile during a trial performed at 600 °C. Temperature fluctuation was found to be minimal. In addition, the O<sub>2</sub> concentration was far below 1% during the entire trial and, consequently, the process atmosphere was nearly inert. This demonstrates that this technology offers a stable process for biochar production.

The monitoring of major components of flue gas during the trial is shown in Fig. 3. The concentration of CO<sub>2</sub> ranged between 13 and 15%. This range of CO<sub>2</sub> values provides a justification for choosing a mixture of 85% N<sub>2</sub> and 15% CO<sub>2</sub> as the fluidising gas. The concept applied here is that the flue gas may be recycled and utilised as the fluidising gas.

The gas analysis was performed at the stack. The level of SO<sub>2</sub> was observed to be very low (4–10 ppm) in all of our trials. NO<sub>x</sub> was also low and in the range of 120 to 125 ppm while CO was between 40 and 50 ppm (Fig. 3). The concentrations of hydrocarbons were also measured; however, the values were not detectable and therefore, not reported here. These values were found to be well below the emission limits recommended by the Industrial Emissions Directive (IED) 2010/75/EU.

### 3.2. Product distribution of py-oil

The analysis of the scrubber water sample (*i.e.*, product distribution of py-oil) is shown in Fig. 4. The Py-oil components were divided into six major groups, which include polyaromatic hydrocarbons (PAHs), monoaromatic hydrocarbons (MAHs), alcohols, phenols, and C10–C14 and C15–C28 liquid hydrocarbons. This grouping was done following previous studies.<sup>54,55</sup> It was found that the

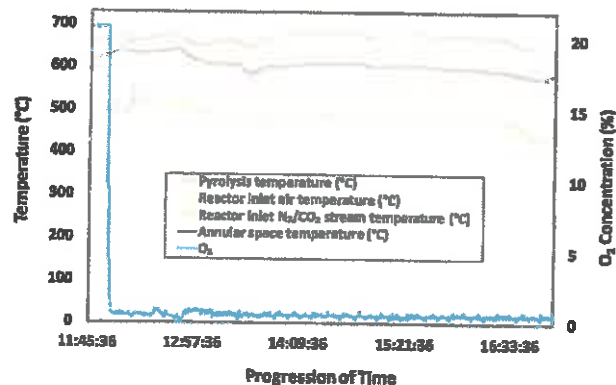


Fig. 2 Temperature profiles and oxygen concentration (in the pyrolysis zone) for the 600 °C trial.

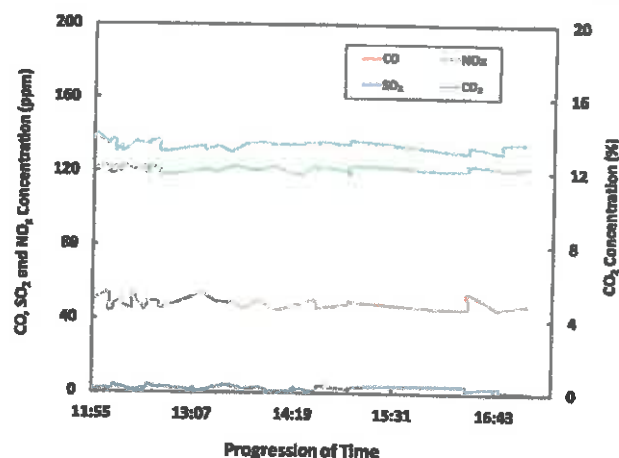


Fig. 3 Analysis of flue gas using an online IR analyser for the 600 °C trial.

production of PAHs and MAHs were minimal in the py-oil sample. The major components of py-oil were hydrocarbons followed by alcohols and phenols. This product distribution is favourable if py-oil is considered for combustion to provide energy to the pyrolysis system.

While the py-oil product distribution is favourable in the context of combustibility, it will still require pre-treatment before it can be used as a fuel in traditional power generators.<sup>24</sup> A better approach could be combusting py-oil to provide energy to the pyrolysis process. In the current semi-pilot plant, a lower combustion temperature was applied with the intention to investigate PFAS destruction. In the real world, a higher combustion temperature could be applied which would combust py-oil and py-gas and provide the required energy to the system.

### 3.3. Yield and stability of biochar

The biochar yield against pyrolysis temperature is shown in Fig. 5. In this study, py-gas and py-oil were partially

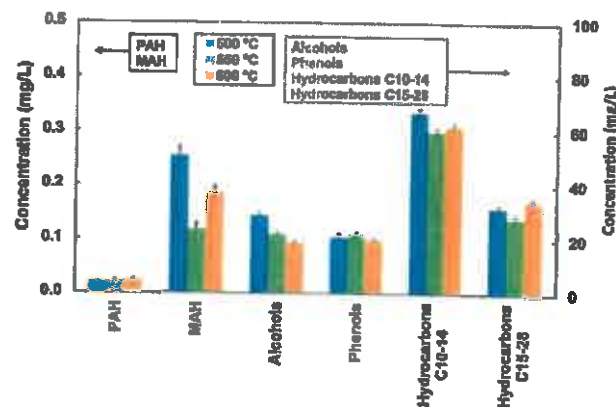


Fig. 4 Analysis of the scrubber water sample (product distribution of py-oil).



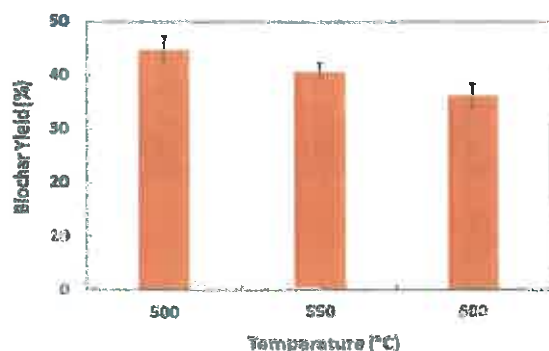


Fig. 5 Biochar yield against pyrolysis temperature.

combusted. The uncombusted py-oil was captured in the water scrubber while uncombusted py-gas was detected in the flue gas. As the combusted portion was not measured, the determination of yields of py-gas and py-oil was not possible. Therefore, biochar yield data are only obtained and presented. Pyrolysis of biosolids results in the decomposition of carbohydrates, proteins, lipids, polyphenols and other macromolecular humic substances as well as microorganisms.<sup>56,57</sup> The level of decomposition of these species increases with pyrolysis temperature, leading to lower biochar yield.

The effects of pyrolysis temperature on biochar formation is further reflected by the proximate and ultimate analyses of the biochar samples (Table 3). As expected, with the increase of temperature, the volatile matter and fixed carbon decreased while the ash content increased. According to the ultimate analysis, C, H and N decreased with the increase of temperature. However, the variation of S was found to be minimal in the investigated temperature regime. This suggests that the sulphur containing species do not degrade significantly within the temperature regime investigated. The proximate and ultimate analyses of biosolids and biochar were also used to construct a Van Krevelen diagram (Fig. S3†). This diagram is an illustration of the maturity/stability of biochar materials.<sup>58</sup> Both H/C and O/C ratios decreased significantly from biosolids to biochar as confirmed in Fig. S3.†

The detailed transition of H/C and O/C values from biosolids to biochar is shown in Table 4. It was found that both ratios decreased with the increase of pyrolysis temperature. A similar result was reported by Fryda and Visser.<sup>59</sup> This was possible because demethylation (loss of

Table 4 H/C and O/C mole ratios of biosolids and biochar

	Biosolids	BSBC-500	BSBC-550	BSBC-600
H/C mole ratio	1.4726	0.6800	0.6761	0.6087
O/C mole ratio	0.4116	0.0125	0.0111	0.0095

BSBC-500: biochar produced at 500 °C, BSBC-550: biochar produced at 550 °C, BSBC-600: biochar produced at 600 °C.

CH<sub>3</sub>) and decarboxylation (loss of CO<sub>2</sub>) reactions are enhanced with the increase of pyrolysis temperature. The increase of demethylation reactions decreases the H/C ratio while the increase in decarboxylation reactions reduces the O/C ratio.<sup>59</sup>

The highest H/C mole ratio was found to be 0.68 for the biochar produced at 500 °C and this value was lower than that from the International Biochar Initiative guidelines (the suggested maximum H/C mole ratio by the guidelines is 0.7).<sup>60</sup> The highest O/C mole ratio was 0.0125 for the biochar produced at 500 °C. This O/C ratio value is in the lower range when compared to that of other biochar samples, and this seems indicative of a very long half-life (more than 1000 years) when added to soil.<sup>61</sup> Therefore, it is worth noting that the produced biochar samples are very stable carbon materials and suitable for soil carbon sequestration.

### 3.4. Biochar morphology and surface area

The morphological analyses of biochar produced at 500, 550 and 600 °C were performed using a scanning electron microscope (SEM) (Fig. 5). It can be seen that a porous structure was evident at all temperatures and the porosity was found to increase slightly with the increase in temperature from 500 to 600 °C. The BET surface area of the biochar samples was measured and the values obtained are in the range of 26 to 55 m<sup>2</sup> g<sup>-1</sup> (mean values were 26.45, 44.06 and 55.29 m<sup>2</sup> g<sup>-1</sup> for the 500, 550 and 600 °C trials, respectively). These values are well aligned with the SEM findings.

The particle size distributions of biosolids and biochar particles are shown in Fig. 7. It was found that the particle size decreases from biosolids to biochar. The median value (for a volume distribution value), D<sub>v</sub>(50), decreased from 829 to 587 μm. D<sub>v</sub>(50) represents the median value for a volume distribution. As shown in Fig. 6, the biochar yield was in the range of 36–45%, depending on temperature. This huge

Table 3 Proximate and ultimate analyses of biochar

Sample	Proximate analysis <sup>a</sup> (%)				Ultimate analysis <sup>a</sup> (%)				
	Moisture	Volatiles	Ash	Fixed carbon	C	H	N	S	O <sup>b</sup>
BSBC-500	1.7	13.2	64.88	19.1	29.27	1.66	3.25	0.46	0.49
BSBC-550	1.3	12.1	66.77	19.4	28.01	1.58	2.78	0.44	0.41
BSBC-600	2.0	10.9	68.03	10.9	27.21	1.38	2.60	0.43	0.35

<sup>a</sup> Values on a dry weight basis. <sup>b</sup> Value determined by difference; BC-500 represents biochar produced at the pyrolysis temperature of 500 °C and similar definitions apply for BC-550 and BC-600.

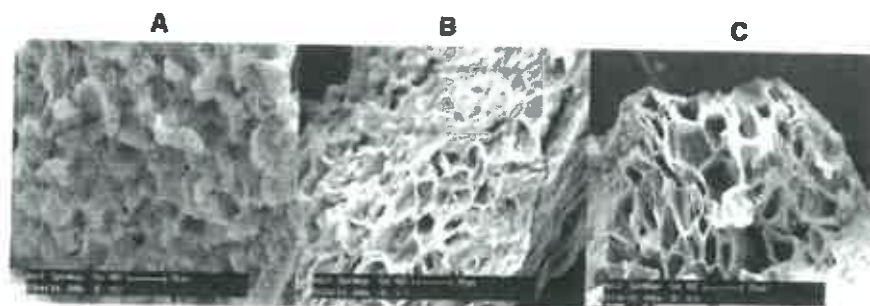


Fig. 6 SEM images of the biochar samples: (A) BSBC-500, (B) BSBC-550 and (C) BSBC-600.

percentage reduction of mass leads to a decrease in solid particle size as confirmed by the particle size distribution results. The bulk densities of solid particles were also reduced. The bulk density of 0.5–2 mm biosolids was found to be  $660 \text{ kg m}^{-3}$ , while the biochar obtained from the pyrolysis of these biosolids at  $500 \text{ }^\circ\text{C}$  exhibited a bulk density of  $620 \text{ kg m}^{-3}$ .

### 3.5. Heavy metal composition

The concentrations of various heavy metals in the biosolids employed and biochar samples produced from the trials are presented in Table 5. Also, the allowable concentrations of heavy metals for land application suggested by EPA Victoria (for biosolids)<sup>62</sup> and the International Biochar Initiative<sup>60</sup> are also provided for comparison. Contamination grade 1 (C1) biosolids, as per the EPA Victoria guidelines, correspond to the highest quality biosolids consisting of the lowest level of heavy metal contamination, and therefore, they are allowed to be used in land application without any specific control measures. In contrast, contamination grade 2 (C2) biosolids are allowed with controlled application.

The mass and volume reduction from biosolids to biochar during the pyrolysis process increased the concentrations of heavy metals. The only exception observed was Hg. This is because of the lower boiling point of Hg, leading to vapourisation of this element at the studied pyrolysis temperatures. While the heavy metal concentrations

increased in biosolids biochar, the values were still below the threshold values of the C2 grade suggested by the EPA Victoria and International Biochar Initiative guidelines.

### 3.6. Destruction of biosolids PFASs

Fig. 8 highlights the PFAS analysis data for biosolids, biochar and scrubber water. While the concentrations of a majority of PFAS species in the biosolids were found to have definite values, all PFAS species were extremely low (less than detectable values) in both biochar and scrubber water. This confirmed that PFASs were vapourised from biosolids at pyrolysis temperature leading to the production of nearly PFAS free biochar. Similar findings were published by Bioforcetech.<sup>63,64</sup> The extremely low concentrations of PFAS species in both biochar and scrubber water suggest that several PFAS species might have been partially or completely destroyed in the integrated pyrolysis–combustion environment maintained in the pyrolysis reactor and its adjacent annular space. Temperature, gas residence time, oxygen, water vapour and the gas phase chemistry of alkali and alkaline earth minerals (*i.e.* K, Na, Ca, and Mg) might have played critical roles in PFAS destruction followed by mineralisation. The roles of temperature and residence time are well-known as higher temperature and residence times can improve the destruction kinetics.<sup>65</sup> The literature has demonstrated that oxygen and water vapour can play critical roles in the destruction of fluorinated hydrocarbons.<sup>66,67</sup> In a similar way, oxygen and water vapour (generated from combustion of pyrolysis gas vapours) can play important roles in PFAS destruction. The release of alkali and alkaline earth minerals into the vapour phase and their gas phase chemistry with PFASs and destructed fluorine can also enhance PFAS destruction and mineralisation efficiency.<sup>66,68</sup> There is also a possibility that PFASs might have converted into some unknown organofluorine compounds which might not be in the analytical range.<sup>26,69</sup> Such compounds could be gaseous organofluorocarbons such as  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ . Unfortunately, the nature of the semi-pilot scale trials presented in this work did not allow the authors to investigate the role of each of these parameters in detail.

Mass balance for PFASs could not be developed for the semi-pilot trials as several PFAS concentration values in the

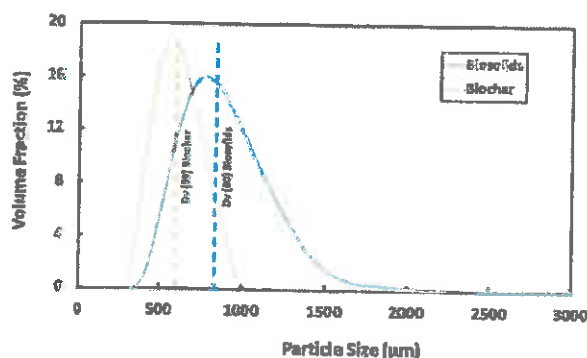


Fig. 7 Particle size distributions of biosolids and biochar.

Table 5 Total metal concentrations ( $\text{mg kg}^{-1}$ ) of the biosolids and corresponding biochar samples

Metals	BS	BSBC-500	BSBC-550	BSBC-600	C1 grade <sup>a</sup>	C2 grade <sup>a</sup>	Biochar guidelines <sup>b</sup>
As	<5	5	5	<5	20	60	13–100
Cd	1.4	1.9	1.6	1.6	1	10	1.4–39
Cr	24	44	50	78	400	3000	93–1200
Cu	660	1100	1200	1100	100	2000	143–6000
Pb	19	40	42	39	300	500	121–300
Hg	0.79	<0.05	<0.05	<0.05	1	5	1–17
Ni	18	37	68	180	60	270	47–420
Se	6	6	6	5	3	50	2–200
Zn	870	1600	1700	1700	200	2500	416–7400

BS: biosolids. <sup>a</sup> EPA Victoria Biosolids guidelines. <sup>b</sup> International Biochar Initiative guidelines. <sup>60</sup>

liquid and biochar samples were not specific. However, attempts were made to gain some understanding on PFAS removal efficiency (Table S2†). In this estimation, the concentration values, shown with the '<' sign in Table S1† (also presented in Fig. 8 with a marker), were considered as the final concentration values for PFASs. For instance, the concentration of PFOS in biochar was  $<0.0002 \text{ mg kg}^{-1}$  (Table S1†). In the estimation, the concentration of PFOS was considered as  $0.0002 \text{ mg kg}^{-1}$ . This estimation provides the removal values of PFBS, PFOS, PFPeA, PFHxA, PFHpA and PFOA as follows: 74, 98, 75, 84, 54 and 96%, respectively. While this is a very rough estimation, this still tells that several PFASs were removed in the pyrolysis process. The removal of other PFAS compounds was either low or they were forming during the process.

To confirm this as well as to explore the mechanism of PFAS destruction, more scientific experiments would be required in the future. As described previously, closing the mass balance for all PFASs was extremely difficult due to the low values of PFASs in the initial biosolids samples. A practical method for the way forward could be performing systematic spiking experiments (*i.e.* spike different PFASs into biosolids) in a lab-environment in a more controlled

manner as spiking at a semi-pilot or pilot scale can be very challenging. Lab-scale spiking experiments in a controlled environment may help not only in closing the mass balance but also in exploring the reaction mechanism of PFAS destruction in biosolids pyrolysis, where the feed material is highly heterogeneous, including organic and inorganic materials.

From this study, the authors would like to highlight that PFASs in biosolids, when compared with pure PFASs, might not require higher temperatures (*i.e.*  $\sim 1000 \text{ }^\circ\text{C}$  for pure PFASs<sup>70</sup>) for their destruction due to the different gas-phase chemistry and potential catalytic effects of minerals/heavy metals present in the biosolids. More scientific work will be required to investigate this fundamentally. Specifically, spiking experiments with particular PFAS compounds at the lab scale in a controlled environment are desirable to evaluate the destruction and mineralisation efficiency and mechanism.

### 3.7. PFAS adsorption

The adsorption efficiency (% adsorption) of char materials for PFASs of contaminated water samples (*i.e.*, sample 1 and sample 2) is shown in Fig. 9. For this study, BSBC-600 and BMBC-600 were used. It is well known that pH has a great impact on the adsorption of PFASs.<sup>22,71</sup> This has also been reflected in the present study. For example, there was a higher PFOS adsorption efficiency for sample 1 compared to that for sample 2. This was due to the lower pH of sample 1 than that of sample 2 (4.3 vs. 7.85), and this is consistent with the literature.<sup>71</sup> At low pH of the contaminated water sample, electrostatic attraction between the positively charged adsorbent surface and the negatively charged PFOS molecules is strong,<sup>72</sup> and this assists in enhanced adsorption of PFOS molecules.

The length of PFAS chains has significant impacts on PFAS adsorption. Short-chain PFASs are difficult to adsorb by many adsorbents, including commercially available granular activated carbon (GAC). For example, perfluorobutanesulfonic acid (PFBS) is a C4 PFAS. The adsorption efficiency of these species by both BSBC and BMBC is low with a range of 19–27% (Fig. 9a). However, the adsorption efficiency of PFBS was

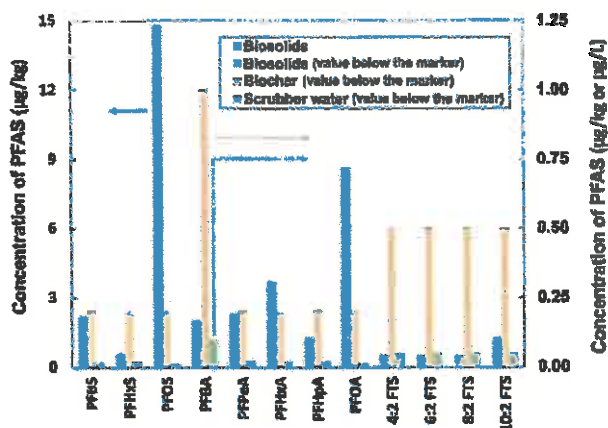


Fig. 8 PFAS concentration data for biosolids ( $\mu\text{g kg}^{-1}$ ), biochar ( $\mu\text{g kg}^{-1}$ ) and scrubber water ( $\mu\text{g L}^{-1}$ ). Columns with markers represent values less than the marker values (see detailed data in Table S1†).



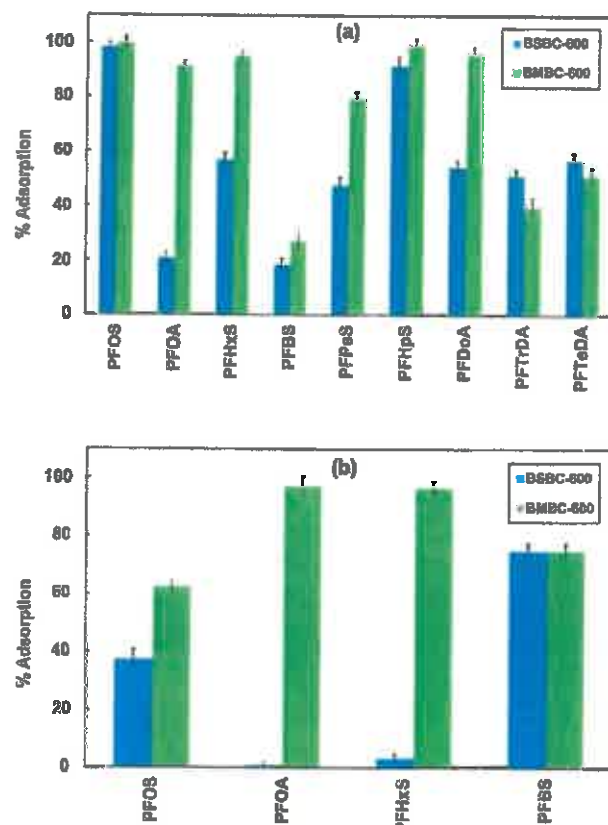


Fig. 9 PFAS adsorption efficiency by various char samples: (a) contaminated water sample with high concentration (i.e., sample 1) and (b) contaminated water sample with low concentration (i.e., sample 2). Note that BSBC represents biosolids biochar, and BMBC represents biomass biochar.

found to increase for the low concentration sample with both adsorbents (Fig. 9b). Using the BSBC adsorbent, the effect of concentration on the adsorptions of PFOS, PFOA and PFHxS was found to be the opposite of that for PFBS. With the decrease of concentration, the adsorption of the three PFASs decreased when BSBC was applied. The impact of concentration on PFAS adsorption with BMBC was found to be relatively low. This is most likely due to the higher surface area of BMBC (BET surface area, BMBC-600:  $79.87 \text{ m}^2 \text{ g}^{-1}$ ; BSBC-600:  $55.29 \text{ m}^2 \text{ g}^{-1}$ ). This finding is aligned with a previous study conducted by Bentley *et al.* who investigated micropollutant adsorption using biosolids biochar and pine biochar.<sup>73</sup>

The terminal functional groups may have an impact on PFAS adsorption. Regardless of concentration, BSBC underperformed in PFOA adsorption when compared to BMBC. It appears that PFASs with carboxylic acids as functional groups have lower adsorption affinity to BSBC. However, the difference of adsorption affinity between BSBC and BMBC becomes very low for PFASs with sulphonic acids as a terminal functional group.

The hydrophobic interactions between PFASs and the adsorbent can assist in PFAS removal from contaminated

water as a hydrophilic functional group with a hydrophobic tail is present in PFASs.<sup>74,75</sup> Briefly, the hydrophobic surface of adsorbents enhances PFAS adsorption.<sup>76,77</sup> The metal content was higher in BSBC compared to BMBC. Therefore, it may be possible that the metals in BSBC reduce surface hydrophobicity and decrease the adsorption of PFASs.<sup>78</sup> This may be the reason for the higher PFAS adsorption on BMBC compared to that on BSBC. While BSBC did not perform as effectively as BMBC for adsorption of some PFASs, its production is expected to be comparatively less expensive. Therefore, a higher amount of BSBC can be applied solely or in combination with BMBC and high performing PFAS adsorbents such as GAC and resins. Also, selective application of BSBC for the adsorption of some PFASs such as PFOS and PFBS can also be considered.

## 4. Conclusions

A semi-pilot pyrolysis unit was employed for the transformation of biosolids into biochar. The semi-pilot unit achieved highly stable thermal and oxygen profiles in the pyrolysis zone. It was observed that with the increase of pyrolysis temperature, the biochar yield and fixed carbon in biochar decreased. It could be noted that the development of pores increased with the pyrolysis temperature. The produced biochar samples were stable and are expected to present a long half-life if used as soil additives. The heavy metal concentration in biochar increased, but it was within the EPA Victoria C2 biosolids grading and the guidelines provided by the International Biochar Initiative. The trials also demonstrated that integrated low-temperature pyrolysis-combustion might be an effective method for removing PFASs from biosolids by converting them into biochar. More scientific experiments in a controlled lab-environment are needed to confirm this.

Biosolids biochar was found to be an excellent adsorbent for removing PFASs from contaminated water. The benchmarking with biomass biochar suggested that the biomass biochar performed better in adsorbing PFASs when compared to the biosolids biochar. Despite this, the lower production cost of biosolids biochar might still make it attractive to be used at a commercial scale.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

The authors wish to acknowledge the financial support received from South East Water, Intelligent Water Networks (IWN) and RMIT University.

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