

# HIGH TEMPERATURE PYROLYSIS FOR ELIMINATION OF PFAS FROM BIOSOLIDS

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**Institute for Chemicals and Fuels from Alternative  
Resources (ICFAR)**

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## What are PFAS?

Per- and Polyfluoro Alkyl Substances (PFAS) are a series of man-made chemicals that have been traditionally used in fabrics and industrial materials with non-stick and oil/water repellent properties, such as carpets, food packaging, Teflon coatings, and fire-fighting foams [1]. Given that PFAS molecules are structures with short and strong Carbon-Fluorine chemical bonds (the strongest bonds in chemistry) with functional groups containing oxygen (O), hydrogen (H), nitrogen (N), and sulfur (S), they are extremely stable and, as such, they have been called “forever chemicals”. They do not break down in the environment, they move through soil, groundwater and surface water, they contaminate drinking water and bioaccumulate in fish, wildlife and humans, with clear evidence of ecotoxicity and human toxicity on growth and development, liver, thyroid and reproductive system.

There are nearly 8,000 types of PFAS compounds, including short and long-chain compounds, with their hydrophobicity and toxicity increasing with chain length. They are named based on their characteristics with the PF as a root, followed by an indication of their chain length and their associated functional group (carboxylic (A) or sulfonate (S)): for example, PFBS (chain length: 4, sulfonate); PFHxS (chain length: 6, sulfonate); PFOA (chain length: 8, carboxylic); PFOS (chain length: 8, sulfonate); PFDODA (chain length: 12, carboxylic), and so forth... Additional names include EtFOSE, EtFOSAA, MeFOSAA, GenX, and others.

In consideration of toxicity, recalcitrance, and persistency of PFAS compounds, the United States Environmental Protection Agency (US EPA) decided to phase out both PFOA and PFOS in 2000 and mandate the complete elimination of PFOA in 2016 [2]. In 2009, the US EPA set a lifetime health advisory level (LHA) to an individual maximum of 70 ng/L (ppt) in drinking water for both PFOA and PFOS, excluding other PFAS types [3]. Likewise, the European Union (EU) targeted a limit value of 100 ng/L in 2019 for the sum of 16 PFAS in drinking water [4].

## PFAS elimination

We know that we have PFAS in our environment, but not necessarily where they are and how best to treat them. Therefore, we need to develop methods for detection, monitoring and treatment in wastewaters, drinking water and biosolids. Granular activated carbon (GAC) has been identified as a reasonably effective adsorbent for PFAS in water streams, although not very efficient in the adsorption of the short chain PFAS family compounds [5].

In the case of biosolids, thermal treatment technologies can use the high temperatures to destroy the PFAS chemical structures by breaking the Carbon-Carbon and Carbon-Fluorine bonds. Thermal processing, such as combustion, pyrolysis, gasification, and hydrothermal liquefaction, are considered as emerging technologies under development and, consequently little is known about their PFAS destruction performance during biosolid waste treatment [6]. Incineration usually occurs at temperatures ranging between 1600 and 2000 °C and has been shown able to eliminate the PFOA and PFOS adsorbed by granular activated carbon (GAC) [7]. The side effect of this method is the formation of harmful emissions with long lifetime effects, such as dioxins and furans [8].

## High Temperature Pyrolysis for PFAS elimination from biosolids

Pyrolysis is a thermochemical conversion method of upgrading biomass ‘wastes’ (including PFAS-containing biosolids and sewage sludge) into valuable solid and gaseous products, commonly called biochar and pyrogas, by heating the feedstock to intermediate or high temperatures (between 500 – 850 °C) in the absence of oxygen or in the presence of sub-stoichiometric oxygen. Biochar is the solid component produced during pyrolysis of biomass. The carbon within biochar structure is incredibly stable (cannot degrade or release into the atmosphere), making biochar a suitable option for soil amendment and carbon storage.

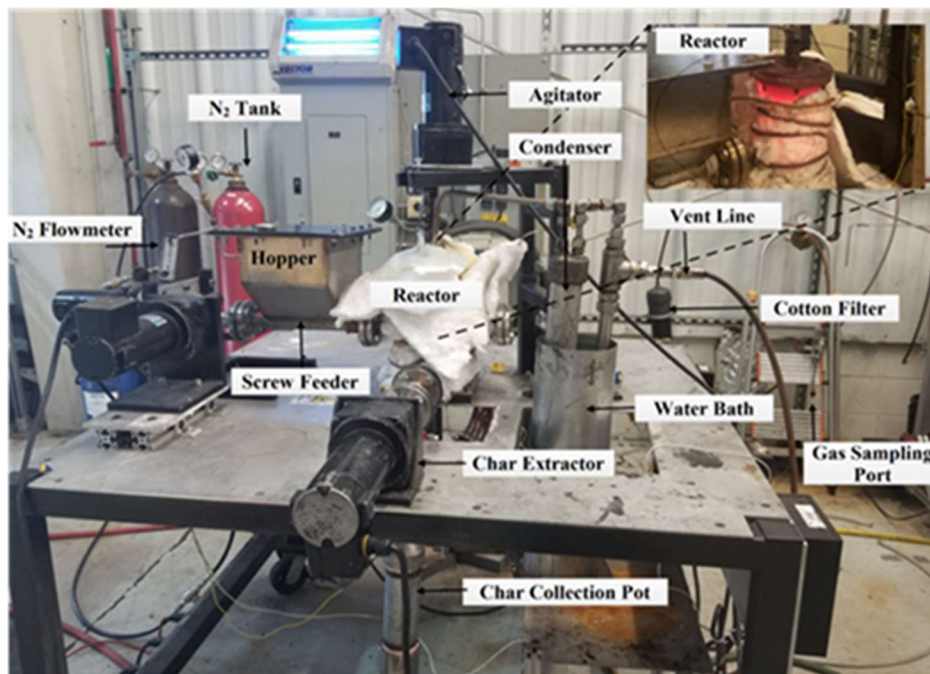


Biosolids

Biochar

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,

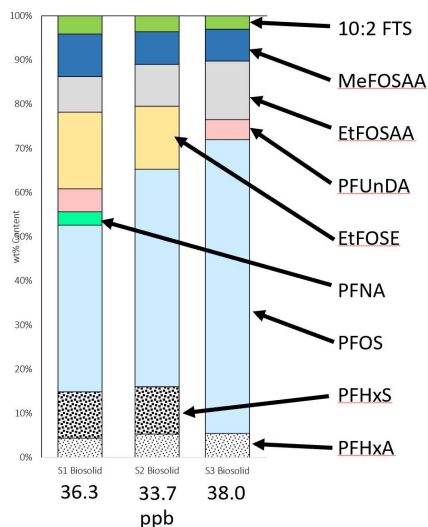
mixed bed reactor, processed biosolids from three water resource recovery sites (S1, S2, S3) across the US under pyrolysis temperatures of 500 and 700 °C.



ICFAR's Pyrolysis Pilot Plant


## Results and discussions

The average concentration of PFAS compounds in the biosolids tested was 36 ppb or  $\mu\text{g}$  per kg, considering the major contribution of Perfluorooctane sulfonic acid (PFOS) among the total detected PFAS compounds:



PFAS compounds in biosolid samples

Some of the physical/chemical properties of the PFOS are:

PFAS Acronym	Molecular Formula	Molecular weight (g/mol)	Chain Length	Molecular Structure	Density (g/cm <sup>3</sup> )	Boiling Point (°C)	Water Solubility (g/L)	Vapor Pressure (Pa)
PFOS	C <sub>8</sub> HF <sub>17</sub> SO <sub>3</sub>	500.13	8		1.84	>400	1.52-1.57	6.7

Molecular structure color codes: Carbon: gray; Hydrogen: white; Oxygen: red; Fluorine: green; Sulfur: yellow

After pyrolysis performed at 500 °C, PFAS compounds were completely removed from the biochar in the S1 sample, and up to 98.7 wt% in the S2 and 97.3 wt% in the S3 biochars. Further reduction was achieved by pyrolyzing the biosolids at 700 °C, with PFAS undetected in the S1 and S3 biochars and reduced by 99.6 wt% in the S2 biochar.

BIOCHAR			
	Values in ppb	500 °C	700 °C
BIOSOLIDS	S1	36.3	0
	S2	33.7	0.44
	S3	38.0	1.07

PFAS concentrations in biosolids and biochars (ppb)

The pyrolysis product yields at 500 °C were 40%, 40% and 20% and at 700 °C they were 30%, 33% and 37% for biochar, biooil and pyrogas, respectively. The amount of PFAS in the gas- and liquid-phase outputs were also measured for the pyrolysis of the S3 biosolids to gain a better insight into the fate of PFAS in all product streams. Please note that, taking into account the yields, to perform a proper comparison, all concentrations are referred to the original mass of biosolids.

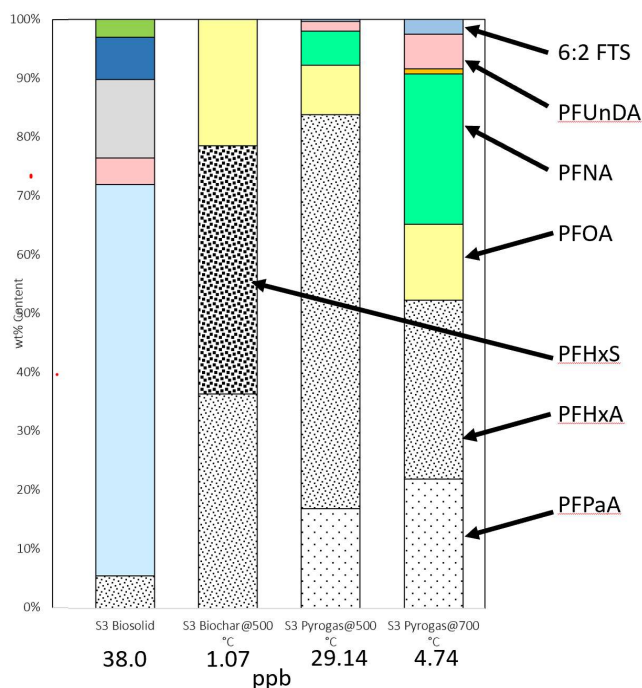
At both pyrolysis temperatures, all detectable PFAS components were eliminated from the biooil fractions of sample S3.

However, the pyrogas still contained 72.9 wt% of total PFAS present in the S3 original biosolid after processing them at the lower pyrolysis temperature of 500 °C. The higher temperature of 700 °C had the noticeable ability to both volatilize and destroy the PFAS compounds (only ~11.8 wt% of the original PFAS was detected in the gas).

Most of the remaining PFAS after pyrolysis existed in the gas phase; that is, ~96 and 100 wt% of the remaining PFAS was segregated in the pyrogas after the pyrolysis at 500 and 700 °C, respectively.

Of the PFAS constituents which are measurable in the biosolids, 10:2 FTS, PFOS, EtFOSAA, and MeFOSAA were all disappeared from the solid phase of the S3 sample at both test temperatures, and additionally were not present in the pyrogas or biooil, indicating both volatilization and decomposition.

The figure below represents each PFAS components in the biosolids, biochar, and pyrogas in terms of their percentage contribution and their concentrations:



PFAS compounds in biosolids sample S3, biochar and pyrogas and their concentrations

Short chain PFAS are characterized by a black dotted bar, while colored columns illustrate the long chain ones. After pyrolysis, most of the long chain PFAS were distinctly converted to short chains. Approximately 85 wt% of the PFAS in the S2 and 95 wt% of the PFAS in the S3 biosolids were composed of long chain PFAS, which were reduced to less than half in all product streams, particularly at the higher pyrolysis temperature. From the environmental point of view, the presence of shorter chain PFAS in biochar is less concerning because they are less toxic.

Overall, it is evident that less harmful products were generated after the pyrolysis process. For instance, PFOS, one of the most stable chemicals [9], was totally eliminated from all samples of biosolids at both pyrolysis temperatures. High melting/boiling point and two strong bonds of sulfonic acid functional group (S=O) make PFOS substances more thermally stable and extremely persistent in the environment compared to the PFOA and other PFAS types [10].

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